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COMMITTEE ON

THE CHALLENGES OF

MODERN SOCIETY

DISPOSAL OF HAZARDOUS WASTES

CHROMIUM RECYCLING

Number 52

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This report confines itself to a detailed presentation of the results obtained regarding the chromium cycle in French industry and the pollution problems posed by its utilization and emphasizing those elements that can be easily transposed to other industrial countries. It all reports on the technical means that can be applied in solving these problems, in addition to the difficulties involved in preparing the framework plan centering on the disposal of chromium waste at national level.

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T R E A T M E N T

O F

H A Z A R D O U S

W A S T E

THE CHROMIUM CYCLE

NO. 52

NORTH ATLANTIC TREATY ORGANIZATION

The Chromium Cycle

A report drawn up within the framework
of the pilot study
"Treatment of Hazardous Waste"

Committee on the Challenges to Modern Society
North Atlantic Treaty Organization

September 1976

PRELIMINARY REMARKS

Within the scope of the study conducted by the C.C.M.S. into toxic and hazardous waste, France proposed to make a contribution by carrying out a special study of chromium waste; the choice of such a subject was justified by both the importance of the problem of chromium pollution and the possibilities seen at the time of drawing up a framework plan on the treatment of this waste at national level.

The Ministère de la Qualité de la Vie (Ministry for the Quality of Life) commissioned the SERATRADI company with realizing this study. Its primary objective was to obtain better knowledge of the chromium cycle in French industry and of the pollution involved in its utilization at the various stages of the processing of the mineral, manufacture of the basic products, application of these products and their consumption. At the same time, the various techniques that could be used in solving the problems at issue, in particular those involving water pollution, were to be investigated in detail.

However, by analyzing the chromium cycle, locating where chromium waste occurs in the environment, characterizing such waste and studying the treatment and disposal processes and techniques that can be considered, the ultimate goal sought was to elaborate and implement a framework plan centring on the disposal of chromium waste.

In this respect great hopes have been set in the possibility of having the bulk of chromium waste occurring throughout the country treated in a plant situated in Wattrelos in Northern France. This was the only plant in the country to produce chromium salts for chemical applications and was itself faced with major problems involving discharge of chrome effluents.

In view of the fact that this plant has developed two patented processes for recycling these effluents and possibly those from other industries, it could be hoped that use of Wattrelos as a collective treatment centre serving the region and perhaps even the entire country would be a first step on the way to solving the problem. Unfortunately, the principal activities of this plant have been jeopardized for economic reasons, so we have been forced to reconsider the entire system projected.

As such reconsideration has not yet been completed, the present report will confine itself to a detailed presentation of the results obtained regarding the chromium cycle in French industry and the pollution problems posed by its utilization by emphasizing those elements that can be easily transposed to other industrialized countries. It will also report on the technical means that can be applied in solving these problems, in addition to the difficulties involved in preparing the framework plan centring on the disposal of chromium waste at national level.

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SUMMARY

The MINISTERE de la QUALITE de la VIE (MINISTRY for the QUALITY of LIFE) commissioned SERATRADI with a study aiming at drawing up a detailed balance of the pollution problems linked with the utilization of chromium.

Three chromium groups are concerned:

- metallurgical applications
- chemical applications
- refractory applications.

France has to import all the chromite required by its industry, in recent years roughly 300 000 tonnes annually, as it does not have any deposits of its own.

By studying the losses recorded by these three major groups, it is possible to specify the environmental problems and outline the various means used or projected in effectively controlling pollution.

1/Metallurgical group:

Preparation of chrome alloys for the production of chrome steels and irons.

The losses determined do not have any impact on the environment as they contain chromium in its inert mineral state. These are in particular losses through dust when the mineral is being handled and fed into the furnaces; they can be substantially reduced by developing dispersion-inhibiting and fume-filtration systems.

2/Chemical group:

Chromium compounds have numerous applications. Chromium occurs in the form of toxic CrVI, and also in the form of CrIII, which are found in most effluents.

Surface treatment workshops and tanneries seem to be the source of major chromic pollution.

Prevention or treatment methods are available in the majority of cases but are not as yet employed on a large scale.

3/Refractory group:

Chromium used in the form of chromite is not harmful. The refractory bricks cannot be recovered more than once and the chromium used is thus lost.

Conclusion:

Only the chemical group presents problems of pollution. By way of contrast, mineral losses are recorded in metallurgy. An overall waste disposal plan could be advocated. Indeed, zones and regions where pollution due to chromium VI is disquieting are roughly known. By progressively setting up a disposal system at national level, small and medium-size enterprises could be offered collective means which, technically and economically, should play a leading role in the progressive elimination of environmental pollution caused by chromium.

The table below sums up the consumption of chromite and the chromium losses of the three groups.

Group	Chromite consumed (t per year)	Cr equivalent (t per year)	Cr losses (t per year)
Metallurgy	272 000	90 000	10 200
- ferrochromiums		80 000	
- others		30 000	
Chemistry	29 000	8 700	4 400
- surface treatment		2 000	1 700
- tanneries		1 700	500
- pigments		1 100	7
- others		approx. 4 000	approx. 2 200
Refractories	26 000	6 500	+
Total	327 000	105 000	+ 16 800

\+ It should be pointed out that no losses of harmful Cr are involved in the fabrication of refractories; once they have been completely consumed, they are all discharged in the inert state.

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I N T R O D U C T I O N

In 1797 VAUQUELIN discovered a new metal in an ore stemming from Siberia. He called it "chromium" from the Greek word "χρόμος" (meaning colour) because of the bright colours of its salts.

It was not until 1843 that BECQUEREL first succeeded in obtaining a chrome deposit by electrolysis of a boiling solution of chromium chloride. Chromium already had chemical applications at this period in the fabrication of pigments, as a mordant for wool, and even as an oxidizing agent.

Only in 1923 did SERGEANT discover a method that could be used in industry, namely a bath allowing hard and brilliantly coloured chromium deposits to be obtained by adding $H_2 SO_4$ as a catalyst.

In about 1930, the use of chromite-based refractories began to develop, their resistance to elevated temperatures being highly appreciated in the lining of open-hearth furnaces.

The discovery of other interesting properties, such as high corrosion resistance (through the formation on the surface of a thin, noble, hence passive, metal oxide layer which protects the metal against the effects of the atmosphere) gave rise to a fairly rapid increase in the consumption of chromium in metallurgical applications. From this point on, stainless steels began to occupy an important position in the iron and steel industry. At present it is scarcely possible to imagine doing without chromium as no other metal with equally as good properties has yet been found.

.../

The chemical applications of chromium are in full development in view of the international economic situation or for environmental reasons (effluents):

- Tannery:

Advances made by developing countries where breeding is carried out on a large scale are made at the expense of industrialized countries, which are finding it more and more difficult to import untreated skins from overseas;

- Surface treatment:

Such treatment is making constant progress in industrialized countries but involves a very high percentage of chromium losses in effluents, the progressive reduction of which will probably result in stagnation, and even a reduction, of the consumption of chromic acid;

- Pigments:

They not only face stiff competition from organic pigments; they are also criticized on account of their toxicity.

In 1972, 6.75 million tonnes of chromites were produced throughout the world, representing roughly 2.2 million tonnes of chromium metal. These figures are not all too high if compared to the consumption of other metals, such as aluminium (6.5 million), copper (7 million), iron (450 million).

However, attention has for a long time been devoted to the problems of nuisances involved in the utilization of chromium since the fabrication - or use - of certain products sometimes gives rise to serious pollution.

There are three types of chromium compounds depending on the valence:

- + 2 : chromous compounds
- + 3 : chromic compounds
- + 6 : chromates.

.../

The highly unstable chromous state easily assumes the chromic state by oxidation; the chromic state is stable and not harmful. On the other hand, compounds containing hexavalent chromium are highly toxic on account of the oxidizing properties of CrVI.

A great deal of research work has been embarked upon in order to study means of detoxicating chromium-containing effluents and possibly permit the metal to be recovered.

Pollution, treatment, recovery - three key words in this study. An attempt will be made to locate at which levels pollution occurs and which effects it has on the environment; then an examination will be made of the technical means of limiting such pollution.

Finally, after an attempt at putting figures to the losses causing pollution, it will be seen to what extent a programme can be initiated so as to provide better control and, if possible, eliminate the major sources of pollution.

1. PRODUCTION AND CONSUMPTION OF THE MINERAL

Chromium is found in nature in the form of chromite ores. These contain varying proportions of different metallic oxides such as Al_2O_3, MgO and above all FeO. All of this constitutes a chromium aluminate of iron and magnesia:

$$(Fe, Cr, Al)_2 O_3 - (Mg - Fe) O$$

known as a mineral of the spinel group.

1.1 Types of ores

The distinction is made between three types of ores whose names reflect their subsequent utilization.

- Metallurgical chromite

The following properties are generally required:

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- $Cr_2 O_3$ content $\geqslant$ 47 % ;
- ratio of Cr:Fe $>$ 3 (may vary between 2 and 3 in certain cases) ;
- $Si O_2$ content 8 to 10 % ;
- granulation: rocky ore, minimum of slack.

This type is found in stratified deposits, in stratified ultrabasic complexes (heavy mineral rocks low in Si content); it makes up roughly 25 % of exploitable reserves known.

The production yield is linked with the physical appearance of the ore, which must be as bulky as possible; in this way supply is confined to specific types of ores. The average price (cif) was approximately 250 Francs per tonne in 1973[+].

- Chemical chromite

Chemical chromites are available in several qualities. Depending on the projected application, these chromites can have different characteristics. However, the criteria involved are on average as follows:

- $Cr_2 O_3$ content $\geqslant$ 45 % ;
- ratio of Cr:Fe $\simeq$ 1.6 ;
- $Si O_2$ content 5 to 8 % ;
- granulation: fine and friable ores, concentrated; known as "reactive chromite".

This type is likewise found in stratified deposits in basic complexes (endogenic rocks with an Si content of less than 55 %), stratified in shields (Bushveld in South Africa, for instance). It is estimated that chemical chromite makes up 65 % of the world's reserves.

Finely divided ores are perfectly suited for the production of chromium salts as the chemical attack on the slack is easier. This explains the fact that when ores of average

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[+] Journal du Four Electrique - August 1973.

.../

concentration are employed, the prime costs of this chromite are lower (175 Francs per tonne cif in 1973)[+].

- Refractory chromite

Characteristics:

- $Cr_2 O_3$ + alumina > 57 % ;
- ratio of Cr:Fe ≃ 2.5 Iron < 10 % ;
- $Si O_2$ content ≃ 5 % ;
- Mg O < 15 %.

Refractory chromite, which represents roughly 10 % of the world's reserves, is found in fairly abundant quantities in solid ore deposits in the ophiolitic complexes of orogenic belts (Urals, Turkey, Mindanao in the Philippines), average price: 100 Francs cif in 1973.

Open-cast mining is practised at the deposits of the three types of chromites. The pure chromium content of the ore is generally greater than 20 %; the mechanical preparation work following extraction (washing, elimination of sterile matter) increases this content appreciably.

1.2 Producer countries

Table 1 reveals that 5 countries make up roughly 85 % of worldwide production and possess 99 % of known reserves. (It should be noted that the reserves of USSR are without doubt far greater; unfortunately, no precise figures are available.)

In addition to the five major countries (South Africa, USSR, Turkey, Philippines and Southern Rhodesia), the "other countries" worthy of being noted include India, Iran, Madagascar, Sudan and Brazil.

[+] Journal du Four Electrique - August 1973.

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Another potential source of chromium can be mentioned: the eruptive rocks of the Earth's crust. It has been calculated that rockmining would permit 30 kg of chromium to be extracted from 100 tonnes of eruptive rocks...

Although this is not impossible technically, the cost of such a process and the aesthetic nuisances caused rule out this approach in the foreseeable future.

TABLE 1

PRODUCTION AND WORLD RESERVES OF CHROMITE

(in millions of tonnes)

Country	1970	1971	1972	Estimated reserves
USSR	2.2	2	2.6	> 50
South Africa	1.57	1.7	1.7	2 000
Philippines	0.55	0.56	0.4	7.5
Turkey	0.5	0.53	0.65	10
Southern Rhodesia	0.4	0.4	0.4	600
Others	0.7	0.9	1	24
TOTAL	5.92	6.09	6.75	≃ 2 700

.../

1.3 Consumption

The consumption of chromites increases from year to year. The growth rate in EEC countries was 4.5 % between 1969 and 1971. On the other hand, great irregularity has been registered in France.

TABLE 2

CONSUMPTION OF CHROMITES

(in thousands of tonnes)

Year	Country	
	France	EEC
1969	330	1 198
1970	421	1 243
1971	340	1 253
1972	276	
1973	327	

.../

In order to determine the production of chromium to which these figures correspond, the average chromium contents below will be adopted:

- metallurgical chromites 33 % of potential Cr ;
- chemical chromites 30 % of potential Cr ;
- refractory chromites 25 % of potential Cr .

In France, the distribution of chromites in terms of tonnes and depending on their application can be determined as follows (with the chromium equivalence on the basis of the percentages listed above):

TABLE 3

DISTRIBUTION OF THE VARIOUS TYPES OF CHROMITES CONSUMED IN FRANCE

		1972 in tonnes	1973 in tonnes
Metallurgy	chromite	231 000	272 000
	chromium content	77 000	89 000
Chemistry	chromite	25 000	29 000
	chromium content	7 500	8 700
Refractories	chromite	20 000	26 000
	chromium content	5 000	6 500

.../

In terms of percentages, this represents the following distribution:

		1972	1973
Metallurgy	(% of chromite	84	83
	) % of chromium	87	85
Chemistry	(% of chromite	9	9
	) % of chromium	8.5	8
Refractories	(% of chromite	7	8
	) % of chromium	4.5	7

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II BREAKDOWN OF CHROMIUM APPLICATIONS

The bulk of ores imported into France is used in the fabrication of basic products employed in various industrial sectors.

- Ferrochromiums are the basic element in the metallurgical applications of chromium.

- Sodium dichromate and chromic acid form the starting point for chemical applications.

- The refractory industry makes direct use of chromite.

The various forms of production in these three sectors will be examined in turn.

Table 4 gives a general view of the three supply and treatment processes.

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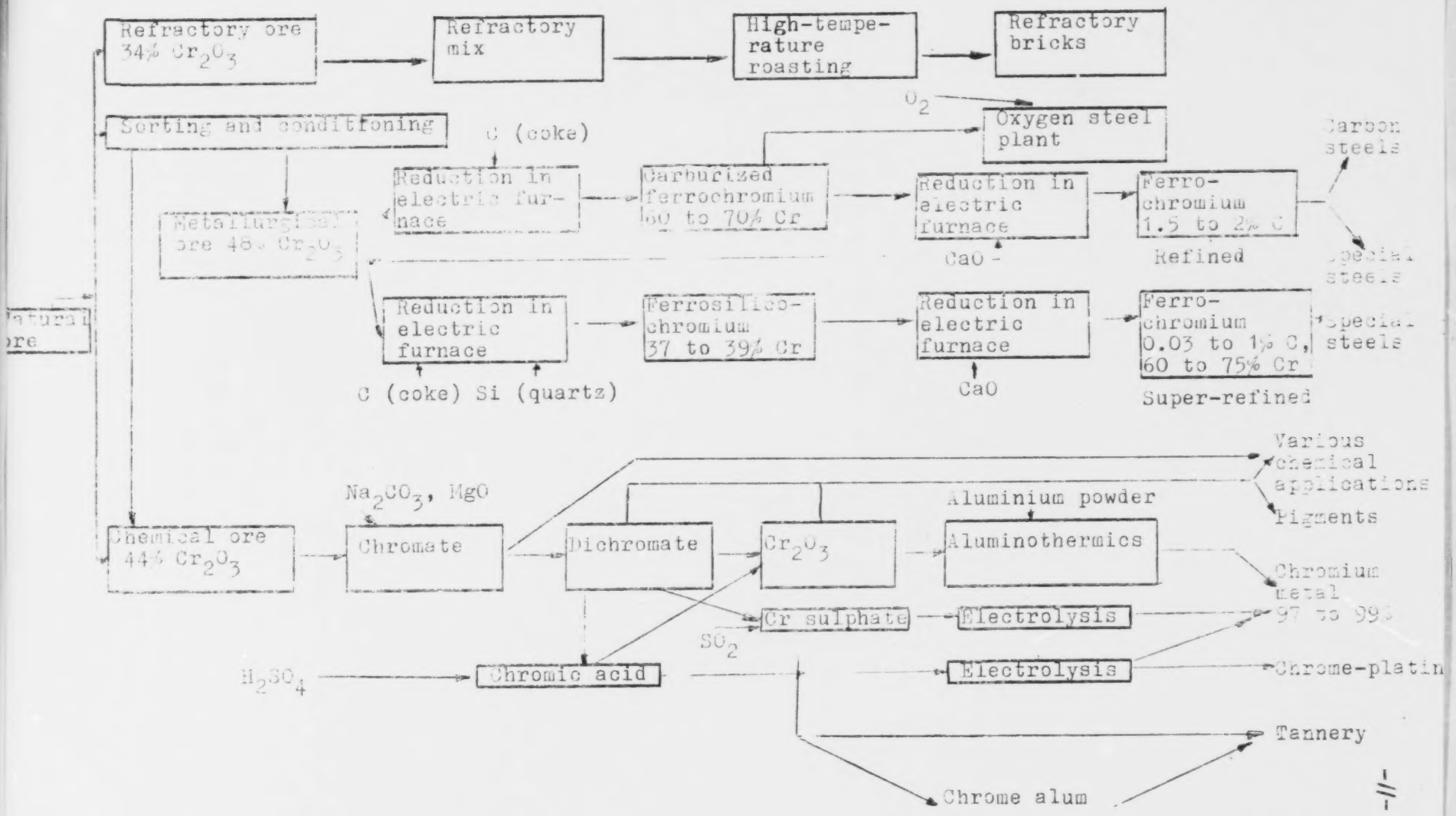
SUPPLY AND TREATMENT PROCESSES



A/METALLURGICAL APPLICATIONS

1. Basic products: ferrochromium and silicochromiums

The distinction is usually made between three major groups of chrome alloys:

- silicochromiums
- carburized ferrochromiums
- super-refined ferrochromiums.

A brief study will be made of the preparation of these three products.

Whatever the intended use of chromite, the handling operations undergone by the ore (unloading, storage, transportation) between the port of arrival in France and the place of utilization are inevitable. The ensuing pollution is not all too visible; nor can it be easily measured, however, and losses through non-harmful dust are estimated as being substantial. When batches are being formed, the chromite is crushed and screened, giving rise to mechanical losses. Chromite losses due to dispersion are estimated at 5 %.

Another loss common to the preparation of all ferro-alloys is caused by the scatter of dust in the flue gases of reduction or smelting furnaces.

These mechanical losses are estimated at 2 %. Adequate equipment could reduce them to less than 0.5 %, the proportion recovered being reutilized after agglomeration with a binding agent.

None of the above-mentioned losses present harmful effects as the dust stems from the ore where the chromium is in an inert, insoluble and hence non-toxic state.

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1.1 Carburized ferrochromium

Reduction is performed with carbon (coke or anthracite). The ore-reducer mix is reduced in an electric furnace. This furnace comprises a cylindrical tank generally with a carbon bed, with 1 or 3 electrodes depending on the power of the furnace. The chromite, coke and flux (often CaO)are fed in at the top.

A carburized ferrochromium is obtained with a chromium and carbon content of 60 - 70 % and 4 - 10 % respectively, depending on the degree of refining desired.

Tapping takes place at the bottom at regular intervals. The slag contains no insignificant share of chromium oxide and reduced chromium metal in the form of droplets. The chromium is in an inert state and constitutes roughly 3 % of the chromium fed in.

The overall yield for carburized ferrochromium is thus roughly 90 %:

• losses due to handling of the ore	:	5 %
• losses in the flue gases from the furnace	:	2 %
• losses in the slag	:	3 %
TOTAL		10 %

1.2 Refined ferrochromium

A ferrochromium of lower carbon content is to be obtained. For this purpose the carburized ferrochromium obtained in the preceding operation is decarburized by reacting it with oxygen either as gaseous oxygen or by adding more chromite ore.

.../

This operation is performed on a discontinuous basis in stationary ore tilting furnaces. The refined ferrochromium obtained, with a carbon content of less than 2 %, is separated from the slag, which contains roughly 2 % chromium.

The overall yield is 88 %:

- 10 % loss for carburized ferrochromium
- 2 % in the slag.

1.3 Super-refined ferrochromium

The silicothermics process is employed to reduce the carbon content to extremely low levels; silicon has a highly reducing effect on the oxides of chromium ores.

Ferrosilicon was first used until it was noticed that a "ferrosilicochromium" could be employed as a reducing agent.

A mixture of chromite, coke and quartz is fed into a furnace identical to those used for carburized ferrochromiums. An alloy containing, for instance, 40 - 45 % Si, 30 - 35 % Cr and less than 0.1 % C is tapped. The silicochromium is used directly by certain steelworkers.

The ferrosilicochromium obtained provides the silicon required to reduce the smelted chromite ore prepared elsewhere, in addition to units of chromium to be found later in the super-refined ferrochromium.+

The production losses through silicothermics can make up 7 % of chromium stemming from the fabrication of silicochromium (2 - 4 %) and final preparation (3 - 4 %).

The overall yield for super-refined ferrochromium is 87 %;

+ Ugine - Perrin process (patented)

.../

- losses due to handling of the ore : 5 %
- losses in the flue gases from the furnace : 2 %
- losses in the slag of silicochromium : 2 - 4 %
- losses in the slag of super-refined ferrochromium : 3 - 4 %

TOTAL ≃ 13 %

1.4 Conditioning

Ferrochromiums are crushed so as to be available in the forms required by customers. Waste caused by conditioning is estimated at 1 %; however, most waste is recovered for recycling in the fabrication of chrome alloys.

1.5 French production of ferrochromium

Assessment of losses in terms of figures

Table 5 provides a brief outline of the preparation of ferrochromiums and the percentages of losses recorded in the various production processes.

In 1973 production in France was as follows:

- 37 000 tonnes of carburized ferrochromium (60 to 70 % Cr);
- 66 900 tonnes of super-refined ferrochromium (70 to 72 % Cr);
- 5 300 tonnes of refined ferrochromium (70 to 72 % Cr);
- 29 000 tonnes of ferrosilicochromium + (30 to 40 % Cr).

+ Sales figures, as a share was consumed directly in the preparation of super-refined ferrochromium.

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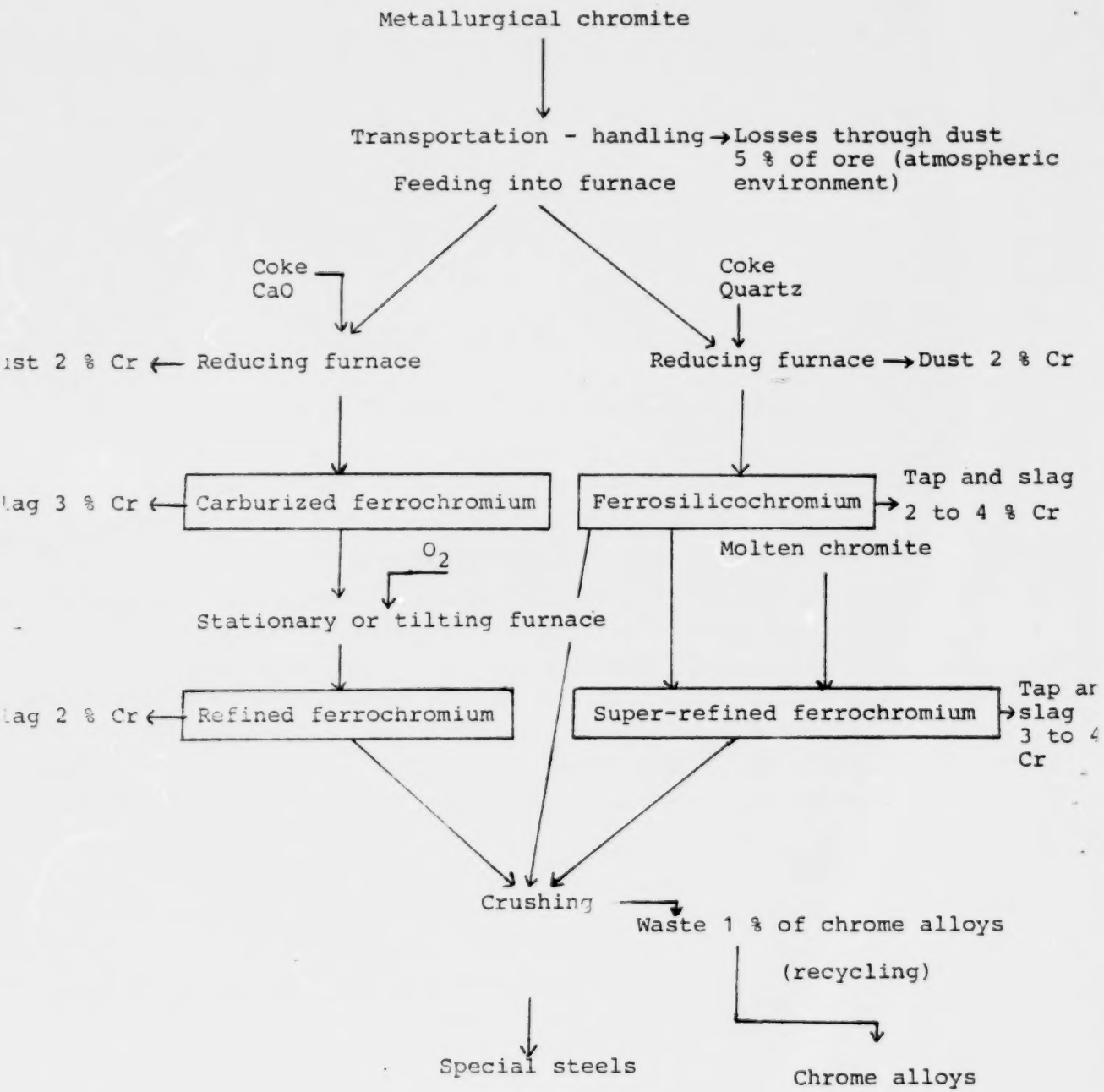
TABLE 5

PREPARATION of FERROCHROMIUMS



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This represents a chromium consumption of roughly 92 500 tonnes and an overall loss of about 10 200 tonnes, 4 600 tonnes of which during handling operations. +

It will be seen in the chapter on means of controlling pollution that industrialists are developing advanced techniques so as to reduce above all losses in the form of dust.

The figures listed above must be viewed as a guide, as the actual consumption of chromium cannot be known in view of the $Cr_2 O_3$ content of ores received in France ranging from 35 to 52 % and the storage system practised, which makes it possible for more or less ore to be used as a function of the quantities of ferrochromium desired.

Losses due to the preparation of ferrochromiums are never harmful. Nevertheless, the desire for better profit-earning capacity and prevention of annoying atmospheric pollution (dust immissions around the plant) call for the development of collection systems.

+ Cf. page 25 ff.

1.6 Location of ferrochromium-producing plants

There are two ferrochromium-producing plants:

- L'Ardoise (Gard) on the banks of the Rhône;
- Moutiers (Savoie).

A plant located in Laudun (Gard) produces only silico-chromium.

As already seen, the ferrochromium industry is faced with a problem when it comes to handling and stocking the ore.

An approach is presented by sheltered storage and by spraying open-air stocks with sticky substances.

Major efforts are currently being undertaken to reduce losses through the flue gases from furnace operations and in this way increase output.

At l'Ardoise, for instance, a plan is being studied with the aim of equipping each furnace with dust extractors with fibreglass shafts (resistant to elevated temperatures). The dust recovered will be reutilized in production.

The study provides for equipping the stainless steel preparation furnaces (also produced at l'Ardoise) with liquid dust extractors. The sludges, mixed with the ferrochromium dust and then dried, could be reemployed as a raw material for ferrochromiums.

It is estimated that these techniques would enable losses by way of flue gases to be reduced to roughly 0.5 %.

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MAP 6

PHICAL LOCATION OF FERROCHROMIUM- AND SILICOCHROMIUM-
ING PLANTS

☆ Ferrochromium and silicochromium

• Silicochromium

.../

2. Utilization of ferrochromiums

2.1 Chrome steels

After the Second World War, the use of chrome steels developed rapidly. The characteristics of the steel are modified depending on the proportion of chromium added; in all cases, however, such additions give it a certain number of interesting properties. They increase its hardenability, increase its processing temperatures, in addition to augmenting its hardness, ultimate tensile strength and resistance to wear; in excess of 13 %, they make the steel stainless.

Ferrochromium is used as an alloying element for these steels. It should be noted that steels alloyed only with chromium are in widespread use (cf. Table 7). Other alloying elements such as nickel, molybdenum and tungsten can also be introduced. Above all nickel-chrome steels are stainless and refractory steels in widespread use (Table 7).

- Preparation:

The bulk of stainless or chrome steels are produced in the electric arc furnace; it should be noted that in some specific cases, the induction furnace is used to obtain a very low carbon content. The furnace is fed with non-alloy iron scrap and lime; fusion takes place at elevated temperatures. Oxidizable elements are burnt and discharged in the slag. Any chromium that may be contained in the iron scrap is in the form of chromium oxides, which are difficult to eliminate (for this reason scraps of chrome steel are avoided).

.../

The slag obtained, which is rich in iron oxides, is removed and replaced by a lime-fluorspar slag. As the environment tends towards reducing, the various alloy elements can be added, including chromium in the form of ferrochromium.

The chromium deads are not insignificant. In addition, this method presents the drawback of not allowing scraps of chrome steel, considered as annoying during initial melting, to be recovered. For this reason there are modified processes:

- the first modification consists of putting chromium scraps in the first batch and then performing oxidizing-fusion without worrying about chromium losses. However, at the end of this first phase, instead of removing the slag, all the oxides that it contains are reduced. For this purpose, powdered ferrosilicon or ferrosilicochromium is added: the chrome oxide is reduced and the chromium reincorporated into the bath;

- a second method consists of doing away with the oxidizing phase and performing fusion in a solely reducing medium without chromium losses. For decarburizing purposes, gaseous oxygen is blown in at a very high temperature ($> 1700^{\circ}$), which first reacts with the carbon, thus enabling a chrome steel of low carbon content to be obtained;

- if very fine special steels are desired, the induction furnace can be employed;

- finally, the technique of mixing in a vacuum, which rules out any losses, is also employed in certain particular cases.

.../

TABLE 7

VARIOUS TYPES OF CHROMIUM-CONTAINING STEEL

STEELS ALLOYED ONLY WITH CHROMIUM	
% of chromium	Utilization, characteristics
1 %	Tools, ball bearings, files
6 %	Cracking tubes
13 %	Cutlery
12 % + 2 % C	Ledeburitic steels for tools
17 %	Ferritic stainless steels
20 to 25 %	Fire grates, furnace muffles

NICKEL-CHROME STEELS		
% Cr	% Ni	Utilization, characteristics
0.8 to 2	1 to 4	Construction steels
1.5 to 3	4 to 6	Self-hardening steels; gears, ammunition, armouring
18	8 to 10	Stainless steels for the chemical industry, decoration
25	13	Refractory steels
25	20	Refractory steels
12 to 18	30 to 40	Refractory steels for furnace elements
12 to 18	60 to 70	Refractory steels for furnace elements specially resistant to the penetration of C
12 to 20	76 to 80	Better metals for heating resistors

.../

The French market for chromium-containing steels can be outlined by the following 1974 figures:

1) As far as stainless steels (average chromium content 17 %) are concerned, the figures expressed in 10^3 tonnes are as follows:

- flat products 200
- long products 80

The distribution percentages between the various outlets were approximately as follows:

	Flat products	Long products
Industrial equipment	53	30
Mechanical engineering	12	-
Individual and collective equipment	13	41
Automobiles	5	16
Transportation (others)	6	4
Construction	6	6
Miscellaneous	5	5

2) As regards other alloy steels with variable chromium contents of between 0.5 % and 12 %, a figure of roughly 700 000 tonnes can be advanced for 1974 for the following three areas of application (construction, ball bearings and tools), the percentages being as follows as a function of the above-mentioned outlets.

	Construction	Ball bearings	Tools
Industrial equipment	6	0.5	24
Mechanical engineering	32	14	45
Individual and collective equipment	2	5	9
Automobiles	53	54	15
Transportation (others)	4	20	3
Construction	1	-	2.5
Miscellaneous	2	6.5	1.5

.../

- Losses and pollution

During the various operations, chromium losses occur in the form of chromium oxide in the slag. However, the quantities lost in this manner are difficult to assess.

During the production of alloy steels, it is estimated that 1.4 tonnes of steel must be produced in order to obtain 1 tonne; the 0.4 tonnes of waste are completely recycled in the preparation process.

The only operation bordering on the problems of toxic pollution is pickling. This is required to free the steel from calamine, an extremely adhesive substance rich in chromium oxides. Pickling is generally performed in an acid bath, the first being a sulphuric acid bath and the second of the fluonitric type (nitric acid + hydrofluoric acid). The chromium content of the pickling baths is fairly variable. These baths are neutralized, the metals contained being transformed into insoluble hydroxides, and then disposed of. If a figure had to be given to the quantities of chromium disposed of in this way in the form of CrIII, roughly 400 tonnes per year would be suitable.

- Chromium consumption

The distinction is made between three main types of chrome steels (Table 8). The average waste is 25 % when the ingots are processed into finished products. The waste is recovered almost in its entirety and refed into the steel-preparation cycle.

Within the scope of the study awarded to SERATRADI by the Ministère de l'Industrie et de la Recherche (Ministry of Industry and Research), we attempted to follow up what becomes of chromium-containing steels in metallurgical applications.

.../

For this purpose, we selected a few typical applications listed in Table 7, above all:

- industrial equipment (chemical industry etc.)
- decoration
- plating and cutlery
- electrical domestic appliances and household goods
- tanks etc.

The results of the investigations can be summed up as follows:

- the percentage of waste varies from industry to industry, fluctuating around 20 to 25 % on average;
- primary waste is sometimes reutilized at its production site, which gives rise to secondary waste. This emphasizes the optimized utilization of chromium-based steels;
- all waste is always refed into the production cycles either directly or via specialists in the recovery of metals;
- the lifetime of the products manufactured varies between 3 and 5 years for the shortest period and is indefinite in many cases. However, the chromium-based steels are always returned to the production cycles.

To sum up, it can thus be said that besides chromium-containing steels immobilized for indefinite periods of time and those which are exported in the form of equipment or manufactured goods, these steels are always returned to the steelworks specialized in the production of such steel alloys.

.../

TABLE 8

PRODUCTION (INGOTS AND FINISHED PRODUCTS)
OF CHROMIUM-CONTAINING STEEL +

(in thousands of tonnes)

- Production (ingots)+

	1969	1970	1971	1972	1973
Stainless steels (austenitic)	246	279	216	232	254
Stainless steels (others)	177	188	191	257	275
TOTAL	423	467	407	489	529

- Finished products (1973)

	Average Cr content	Production	Chromium content
Ferritic steels	17 %	213 000	36 210
Austenitic steels	18 %	189 000	34 020
Refractory steels	15 %	7 000	1 050
TOTAL		409 000	71 280

+ Sources: Statistics of the Ministère de l'Industrie (Ministry of Industry)

.../

2.2 Chrome irons

2.2.1 Irons with a low chromium content (Cr < 2 %)

- Carbon content : 3 %

The cupola charges are normally made up of pig iron or steel scraps, chromium being added by way of more or less carburized ferrochromium. Melting yields chromium deads ranging from 2 to 5 % of the initial content.

2.2.2 Irons with a chromium content of at least 6 %

These irons are prepared in the rotary furnace or open-hearth furnace, and sometimes in the electric furnace either with a central electrode or of the induction type so as to avoid recarburization.

Since the atmosphere in these furnaces is always oxidizing (no recarburization), the chromium deads can reach a relatively high level: 7 to 10 %. The lower the total carbon content is to be, the more refined the ferro-chromiums used.

These chrome irons are generally used on a large scale in the fabrication of components resistant to elevated temperatures (400 to 950°C), to wear due to friction, erosion or abrasion, to corrosion by oxidation and certain chemical substances (concentrated or dilute acids and alkaline solutions).

3. Conclusion

From ferrochromiums, a basic product in metallurgy, stainless and refractory steels are prepared, in addition to chrome irons and certain alloys. Chromium losses are never toxic, except during pickling. Only the problem

of dust - which is not harmful but a source of annoyance - can be considered from the angle of pollution.

Although the utilization of metallurgical chromites represents more than 80 % of French imports, the nuisances caused are virtually non-existent compared to the potential nuisances of chemical applications. By way of contrast, there are considerable quantities of chromium losses in terms of tonnage (consumption of the various stainless steel products also results in non-polluting losses; recovery of chromium scrap already occupies an important position).

At the request of the Ministère de la Qualité de la Vie, it was attempted to include the following in the diagram below:

- an estimation in terms of figures of the chromium losses during the various operations described in the chapter headed "Metallurgical applications";

- a theoretical calculation of the chromium content of chromium-based alloys produced in 1973 and the chromite that would have been required to obtain them, these figures being deduced from the chromium content of all special steels produced in 1973.

The tonnages given inside the boxes are thus theoretical calculated figures. The losses refer to the percentages and tonnages (figures between parentheses) mentioned throughout the chapter.

Simplified diagram of the flows of chromium losses during the various operations described in chapter A: Metallurgical applications, and theoretical calculation on the basis of the chrome content of special steels produced in France in 1973, corresponding chromium content of chrome alloys as well as the corresponding theoretical consumption of metallurgical chromite.

Figures expressed in tonnes of chromium.

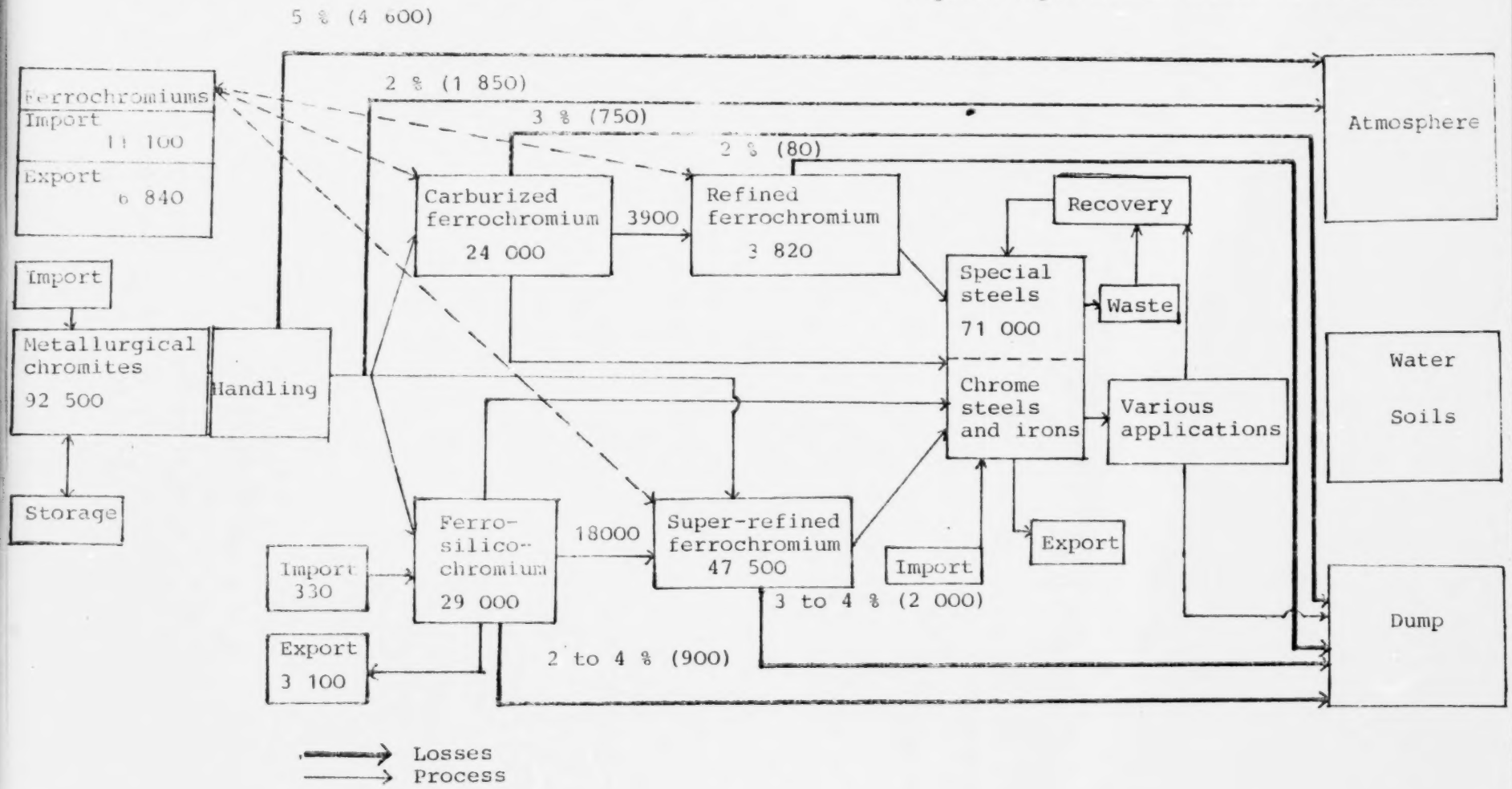

Table 9 attempts to provide a schematic and simplified summary of the various losses recorded in the chapter headed "Metallurgical applications". The restriction was made to quantify that part relative to chrome alloys; the complexity of the steel cycle calls for an in-depth study to be performed within the scope of a study for the Ministère de l'Industrie.

The tonnages indicated (all relating to 1973) were calculated in the following manner:

- the production of the chief chromium-containing steels represents roughly 71 000 tonnes of chromium metal (cf. page 22). On the other hand, the chromium employed for other chrome steels and chrome irons can scarcely be evaluated;

- French production of ferrochromiums and silicochromiums (page 15) enables the quantity of chromium used at this level to be specified; for this purpose the following mean percentage was established in the vicinity of that given by the l'Ardoise plant for the composition of the chrome alloys:

	chromium consumed
• 37 000 tonnes of carburized ferrochromium at 65 % ⟶	24 000
• 5 300 tonnes of refined ferrochromium at 71 % ⟶	3 800
• 66 900 tonnes of super-refined ferrochromium at 71 % ⟶	47 500
• 76 000 tonnes of ferrosilicochromium at 38 % ⟶	29 000

The production of ferrosilicochromium indicated on page 15 represents the sales of ferrosilicochromium (in and out of France); total production reached the level of 76 000 tonnes in 1973, but 47 000 tonnes were used directly in the production of super-refined ferrochromium.

..

- by incorporating into the calculation the percentages of losses at the various preparation phases, the corresponding theoretical consumption of metallurgical chromite can be arrived at from the tonnages indicated earlier.

- Refined ferrochromium : 3 800 tonnes of chromium, 2 % of losses in the slag,
  $\Longrightarrow$ inital chromium $\simeq$ 3 900 tonnes, losses 100 tonnes.

- Carburized ferrochromium : 24 000 tonnes of chromium, including 3 900 for the production of refined ferrochromium and 21 100 directly for steels, 3 % of losses in the slag,
  $\Longrightarrow$ initial chromium $\simeq$ 24 750 tonnes, losses 750 tonnes.

- Super-refined ferrochromium : 47 500 tonnes of chromium, 3 to 4 % of losses in the slag and tap,
  $\Longrightarrow$ initial chromium $\simeq$ 49 500 tonnes, losses 2 000 tonnes.

- Ferrosilicochromium : 29 000 tonnes of chromium, 2 to 4 % of losses in the slag and tap,
  $\Longrightarrow$ initial chromium $\simeq$ 29 900 tonnes, losses 900 tonnes.

The obtaining of ferrochromiums thus called for the consumption of:

- 24 750 tonnes for carburized, refined ferrochromium;
- 29 900 tonnes for silicochromium;
- 49 500 tonnes for super-refined ferrochromium (including 18 000 tonnes from silicochromium);

In all 86 000 tonnes of chromium.

.../

The losses through dust are estimated as a whole at 7 %, while it can be supposed that metallurgical chromites made up roughly 92 500 tonnes of chromium:

- losses through handling : 5 % = 4 600 tonnes,
- losses through furnace dust : 2 % = 1 850 tonnes.

Losses thus total:

- dust: 6 450 tonnes,
- slag, tap: 3 750 tonnes,

Total 10 200 tonnes.

1973 imports and exports of chromium-based alloys were as follows:

	Import	Export
Ferrochromium +	16 616 t	10 206 t
chromium content	11 100 t	6 840 t
Silicochromium ++	891 t	8 204 t
chromium content	330 t	3 100 t

+ Average chromium content 67 %

++ Average chromium content 38 %

B/ Chemical applications

In terms of tonnage, the consumption of chromium in the fabrication of chemical products is clearly less than in metallurgy:

1973 : - 29 000 tonnes of chemical chromites (30 % Cr), i.e. 8 700 tonnes of chromium.

- 272 000 tonnes of metallurgical chromites (33 % Cr), i.e. 90 000 tonnes of chromium.

Nevertheless, the chemical derivatives of chromium constitute this metal's source of toxic pollution. This metal occurs in the hexavalent form (the most harmful) during the fabrication and utilization of numerous derivatives.

Practically all chemical applications are based on sodium dichromate used as a basis in the production of the following main compounds:

- chromic acid
- chromium sulphate
- chromium oxide
- various chromium salts.

Chemical chromite is used almost exclusively for these various applications.

1. Fabrication of basic products

1.1 Sodium dichromate:

Chemical chromite is first crushed, dried and finally ground before being mixed with lime or dolomite and sodium carbonate (reducing mixture enabling better oxidation). This mixture is fed into a furnace before

All these operations take place in a closed circuit, the dust being collected so as to be refed into the cycle.

Roasting takes 1 to 4 hours, the maximum temperature varying between 1100 and 1250°C. The combustion gases are collected and subjected to electrostatic dust extraction after drying. The dust recovered in this way (roughly 15 % of the charge) is returned to the furnace feed mixture.

The losses in the flue gases escaping from the dust extractor are estimated at roughly 2 % of the chromite, but this figure may be reduced to 0.5 % with adequate equipment.

After roasting, the product is introduced into a cooler and then undergoes lixiviation. The sodium chromate is dissolved and separated from the insoluble substances.

Depending on the operational cycle used, the filtration residue can be disposed of, used during the next stage, or partly recycled. If it is not disposed of, it is dried, then crushed in the same way as the chromium ore; the recycled portion is employed in preparing the furnace feed mixture.

The chromium losses are estimated at 20 % of the chromium content of the initial ore. They are due to incomplete oxidation during roasting or partial lixiviation. The non-recycled sterile matter is stored. However, due to its being impregnated by adsorbed chromates and to precipitations, there is a risk of chromium being entrained in the anionic form, which means that impermeable soil has to be provided for disposal

The chromate content of the solution resulting from filtration is greater than 25 %. The alumina also is often dissolved; to eliminate it, it is precipitated in the hydroxide state and then filtered. If necessary, the solution is evaporated until an $Na_2 Cr O_4$ concentration

.../

of 45 to 50 % is reached. There then follows transformation of the chromate to dichromate by means of H_2SO_4 or CO_2 under pressure, in accordance with the following reactions:

$$2\ Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

or

$$2\ Na_2CrO_4 + 2\ CO_2 + H_2O \longrightarrow Na_2Cr_2O_7 + 2\ NaHCO_3$$

The sodium sulphate is recovered in the "cake" containing less than 0.5 % of $Na_2Cr_2O_7$, which is extracted by purification and reintroduced into the circuit.

The filtration and crystallization operations form the last phase.

The final balance enables the following results to be established:

- the production of $Na_2Cr_2O_7$ represents 75 to 85 % of the potential chromium of the starting ore;
- the losses occur chiefly in the Cr^{III} form.

In 1973 French production of sodium dichromate was roughly 18 000 tonnes, i.e. 6 200 tonnes of chromium, so losses can be estimated at 1 500 tonnes of chromium (taking the average figure of 20 % losses during the fabrication of dichromate).

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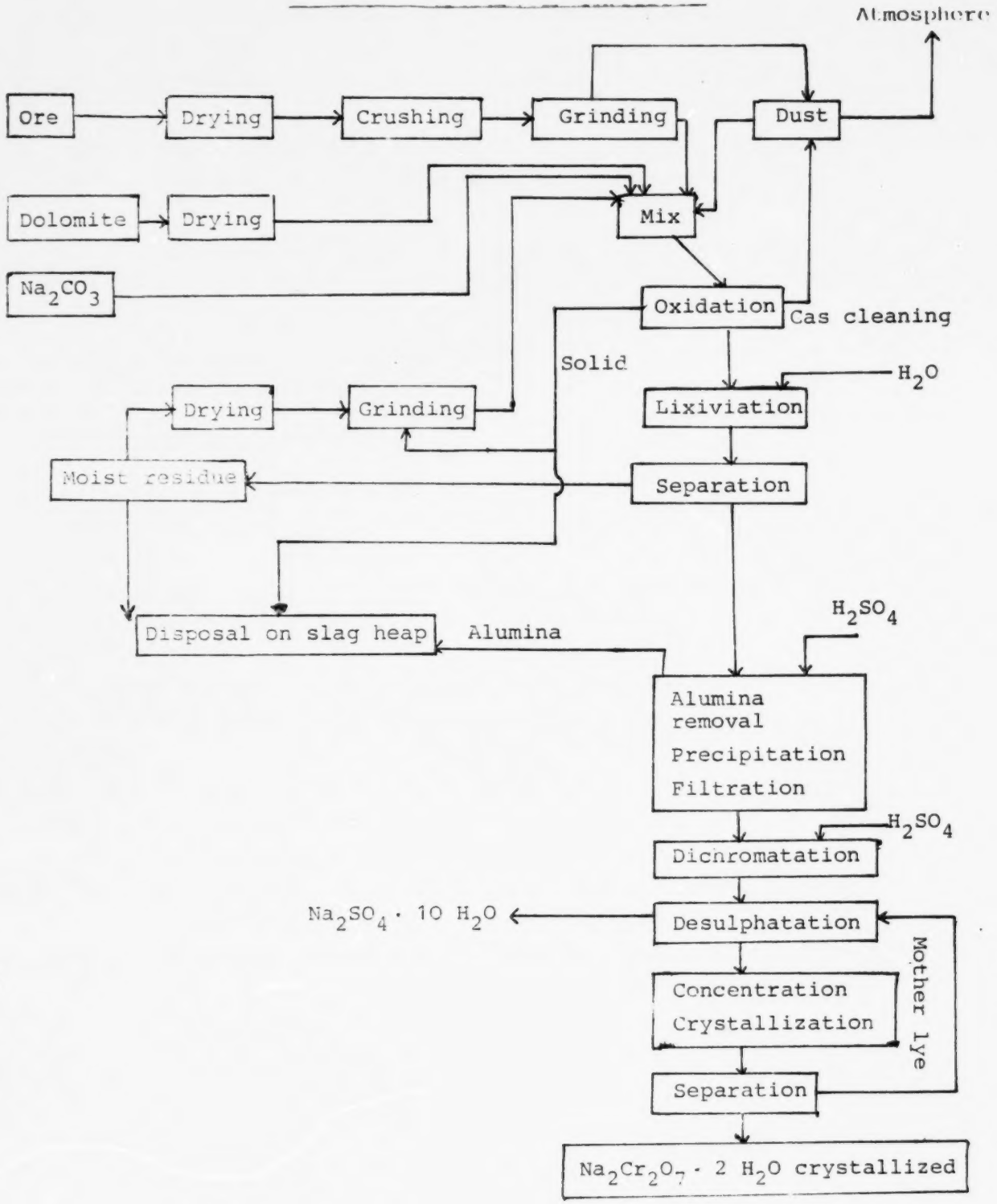
TABLE 10

PRODUCTION of SODIUM DICHROMATE



1.2 Production of other chemical chromium compounds:

Nearly all of these compounds have sodium dichromate as their basic element. It would be long, tedious and of little interest to give the preparation processes of each product; for this reason only the most common will be outlined.

1.2.1 Chromic acid CrO_3: (Table 11)

This acid, which is also known as "chromic anhydride", is a solid, deliquescent substance. It is obtained by reacting H_2SO_4 with a sodium dichromate solution:

$$Na_2Cr_2O_7,\ 2\ H_2O + 2\ H_2SO_4 \longrightarrow 2\ CrO_3 + 2\ NaHSO_4 + 3\ H_2O$$

This operation takes place at a high enough temperature (197°C) for the bulk of the water to be eliminated. The chromic acid and sodium bisulphate are separated into 2 layers at the end of fusion. Roughly 5 % of chromium, reduced during fusion, is found in the bisulphate. Chromic acid is also entrained and is extracted by a "liquid-liquid" process using an organic solvent such as tributyl phosphate+ which, in a very acid environment, traps the Cr^{VI}.

The Cr^{VI} is returned to the sodium dichromate production process (at chromate level). On the other hand, trivalent chromate is neither extracted nor recycled.

1.2.2 Trivalent chromium oxide Cr_2O_3: (Table 12)

A green powder used in obtaining chromium metal, Cr_2O_3 is produced either from the calcination of $Na_2Cr_2O_7,\ 2\ H_2O$ in the presence of a reducing agent (sulphur)

$$Na_2Cr_2O_7,\ 2\ H_2O + S \longrightarrow Cr_2O_3 + Na_2SO_4 + 2\ H_2O$$

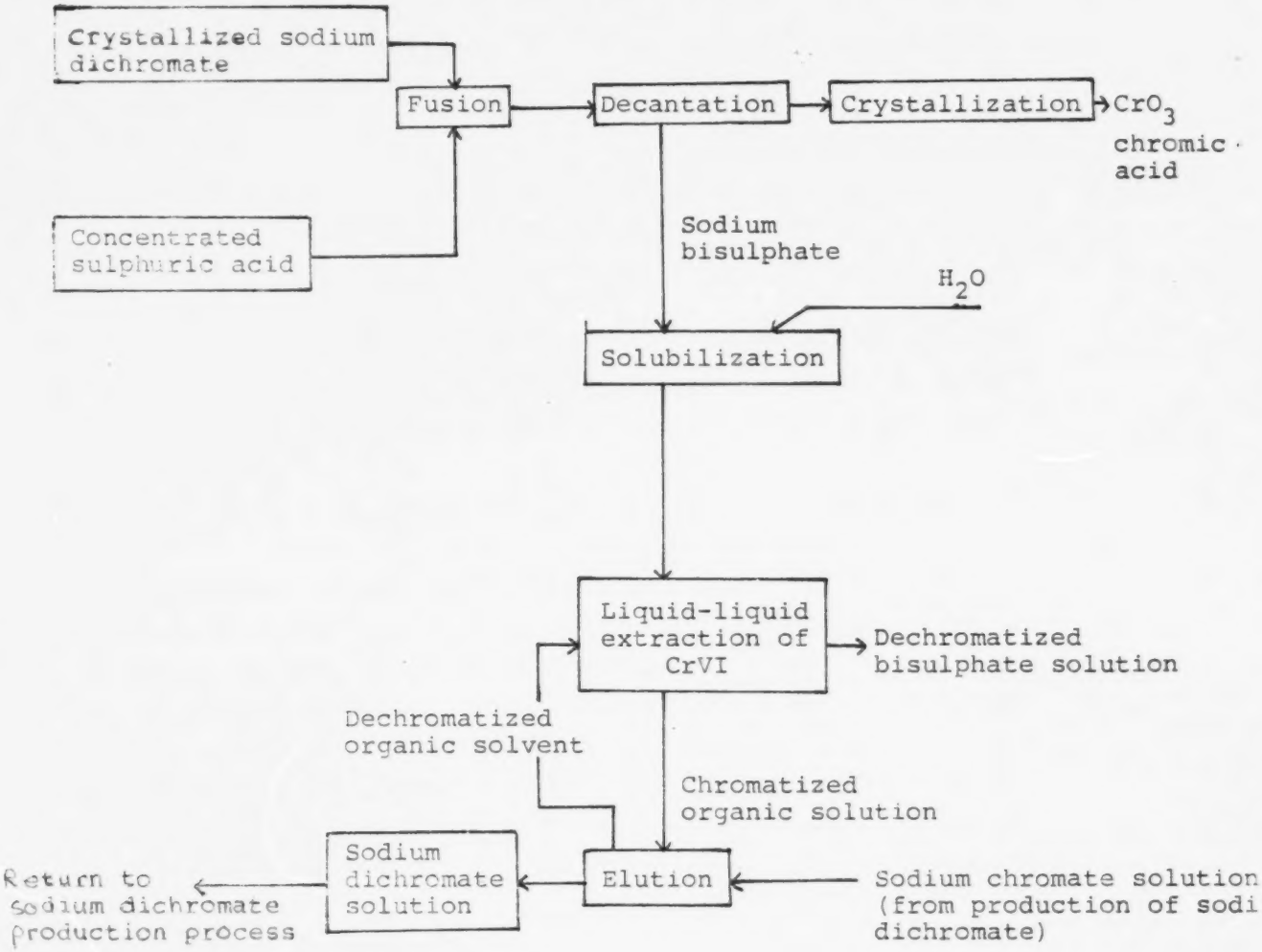
or more generally from CrO_3.

+ Patented process

.../

TABLE 11

PRODUCTION OF CHROMIC ACID



.../

In the first case, reduction takes place in crucibles; the reduction products are collected in extractors and entrained by water. The lyes are then filtered, concentrated and returned to the dichromate production shops.

Cr_2O_3 is collected via a filter press and then dried. Losses occur above all during filtration, so chromate-containing effluents are best recycled.

In the second case, the losses by way of aerosols, which are highly toxic, call for the development of flue gas collecting systems. Some losses occur during the conditioning of Cr_2O_3. Nevertheless, efficiency during processing can be as high as 95 %.

1.2.3 Chromium sulphate : (Table 13)

There are various methods of obtaining chromium sulphate. One of the most common is to react SO_2 and Na_2CO_3 with a sodium dichromate solution. Chromium sulphates having different basicities are obtained:

33° (Schorlemmer) $\qquad Cr \begin{matrix} \diagup OH \\ \diagdown SO_4 \end{matrix}$

66° $Cr_2SO_4\ (OH)_4$

It is estimated that only negligible losses occur during production.

More than 1000 tonnes of chromium are used in the French production of chromium sulphate [+].

It can be seen from this quick survey of the production of the various chromium compounds that the major problems involving pollution stem from the obtaining of sodium dichromate, the basic product.

[+] Figures provided by the Ministère de l'Industrie (Annuaire de Statistiques Industrielles)

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TABLE 12

PRODUCTION OF CHROMIUM OXIDE

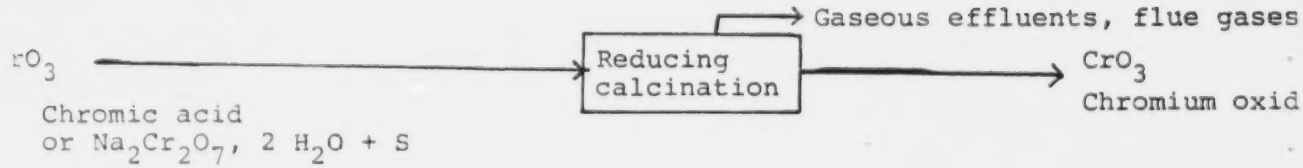
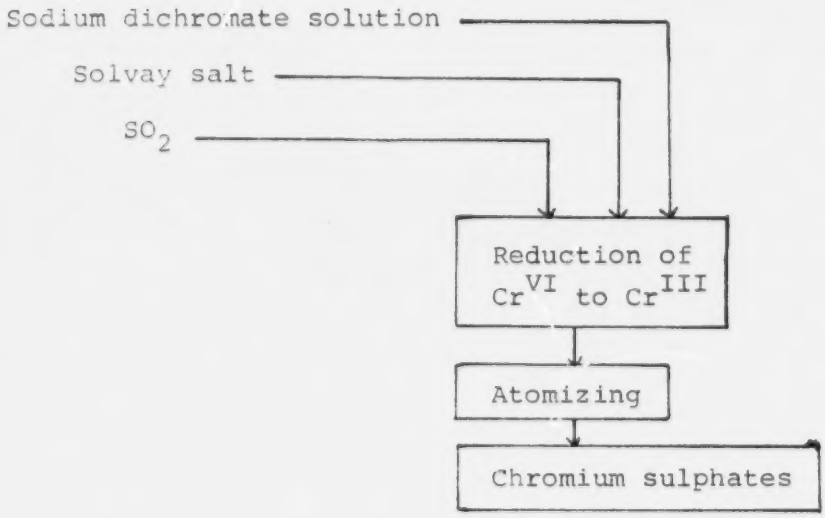


TABLE 13

PRODUCTION OF CHROMIUM SULPHATE



of different basicities

.../

2. Utilization of products

2.1 Chromium in surface treatment:

Possible applications for chromium compounds include providing metals with good corrosion resistance, obtaining a decorative effect, and enabling improved adhesion of paints and varnish.

Two major types of action can be retained: on the one hand, the chemical process of passivation based on the phenomenon of reduction in the reactive bath, and on the other hand the electrolytic process in which the metal to be treated forms the cathode, while the anode cannot generally be attacked and the electrolytic bath is a solution of chromic acid or dichromate to which sulphate anions are added.

Whatever the type of surface treatment, chromium is used in its hexavalent form (chromate, chromic acid) with only traces of trivalent chromium (chrome alum) in some cases; the ensuing pollution is thus highly dangerous, especially as the concentration of discharged effluents can reach high levels.

2.1.1 Pickling (cleansing):

The aim of pickling (cleansing) is to prepare the surface of the substrate for metallization either by eliminating the layer of natural oxide on a metal or by increasing the roughness of the surface of plastics.

Chromic acid is mainly used in three cases together with sulphuric acid:

Aluminium	CrO_3 content	50 to 60 g/l;
Copper	CrO_3 content	200 g/l;
Plastics	CrO content	400 to 600 g/l.

.../

In a solution with an acidic pH value and in the presence of CrVI, metal ions or burr from the plastic are dissolved and there is an accompanying and progressive increase in CrIII.

These impurities call for spent baths to be disposed of after several operations.

Treatment proves to be necessary for effluents with a high CrVI concentration.

2.1.2 Chromating:

Thin but extremely corrosion-resistant layers form on certain metal surfaces immersed in solutions containing chromium VI or III. This has led to large-scale use of chromating processes.

The thin passivation layers formed on zinc and cadmium are most common at the present time.

Solutions of chromic acid (3 to 6 g/l) or sodium dichromate (5 to 9 g/l) are used. During chromating, the hexavalent chromium ions are reduced to the trivalent state and the pH value increases as a result of the consumption of acid. A gel containing a chromium hydrate and chromium chromate forms on the surface of the metal. This deposit takes on various shades depending on the composition of the solution.

The dissolving of Zn or Cd and the formation of chromates in the chromating or passivation bath call for the bath to be renewed fairly regularly. Such a bath containing large quantities of hexavalent chromium is toxic.

Alongside chemical finishing processes (chromating of zinc and cadmium), the same process continues to be used with solutions of chromic acid, hydrofluoric acid and phosphoric acid to form layers containing chromium phosphates which facilitate the adhesion of paints.

.../

This process is employed by the aeronautical and optical[+)] industries and for operations requiring an adhesive substrate for a subsequent coat of paint; this is the case before painting or plastication on aluminium strip (e.g. food cans).

These passivation and corrosion-resistant characteristics are also applied to the protection of silver, with far fewer results, and are sometimes applied to brass, copper or even iron and steels.

A special case is gloss finishing, an operation which enables the gloss of a poor deposit to be improved, in particular for cadmium (chromic acid bath, 150 g/l).

The formation of cadmium chromates does not allow the bath to be preserved as the chromium in the hexavalent form has to be treated prior to discharge.

2.1.3 Mordanting of magnesium:

Chromates give rise to "mordanting" of magnesium (through the formation of a double chromate) making for good adhesion of a coat of varnish. The bath in which components are soaked comprises sodium or potassium dichromate (150 to 200 g/l) and phosphoric acid or other substances.

The development of electrolysis in surface treatment to protect metal objects against corrosion while providing them with a decorative effect makes for the importance of chromium, in particular for chrome plating. However, there are other operations such as electrolytic polishing.

2.1.4 Chrome-plating:

In this case lead forms the anode. The chromium is dissolved in the bath in the form of chromic acid (the concentration varying between 150 and 300 g/l) or dichromate.

+) Use of dark, mat chromate- and carbonate-based layers due to their anti-glare effect.

.../

Chrome alum and chromium sulphate are sometimes added. Sulphuric acid (1 % of chromic acid) is added to facilitate the flow of the current with or without fluosilicate or fluoride ions.

TABLE 14

COMPOSITION OF CONCENTRATED SURFACE TREATMENT BATHS AFTER UTILIZATION

- Pickling (cleansing) baths for plastics

	(1)	(2)
CrVI	212 g/l	165 g/l
CrIII	30 g/l	11 g/l
SO_4	425 g/l	480 g/l
MES	80 mg/l	75 mg/l
Vanadium	5 mg/l	5 mg/l

- Hard chrome-plating baths

	(3)	(4)
CrO_3	30 g/l	112 g/l
CrIII	1.7 g/l	5.2 g/l
SO_4	0.9 g/l	1.4 g/l
Fe	0.5 g/l	5.5 g/l
Cl^-	< 1 mg/l	<40 mg/l
Zn	< 5 mg/l	----------
Pb	ξ	----------

(1), (2), (3), (4) : Analysis of concentrated baths from various shops

.../

The distinction is made between two types of chrome-plating: hard chromium and decorative chromium.

Hard chromium is a thicker (20 μ to 1 mm), hard and dense deposit with a very low coefficient of friction and good corrosion resistance. It is used in the aeronautical and plastics industries, as well as in the fabrication of cutting tools. It also enables worn or spoiled parts to be recovered.

Decorative chromium is only 0.2 to 1 μ thick. This film withstands wear and corrosion.

In all the above-mentioned operations, chromium is deposited on the cathode. For this reason chromic acid must be added to the bath at regular intervals so as to maintain an optimum concentration of CrVI.

After being subjected to electrolysis for 20 to 30 minutes, the workpiece is introduced into a rinsing bath, which means that a certain quantity of concentrated bath is removed (0.15 l/m^2). Depending on the installations, this static rinsing bath or "dead bath" as it is known is treated, partially recycled, or discharged as such in most cases. The chrome-plated parts are rinsed in baths of running water, which carry along the chromium VI residues to the sewers or streams. The chrome-plating electrolyte must sometimes be disposed of after a certain period in view of the formation of salts, hydroxides or other impurities which gradually impair proper functioning of electrolysis.

Entrainment of CrVI in the rinsing water nevertheless constitutes most of the pollution[+]. The hydrogen and oxygen given off at the surface of the cathode and anode respectively form vapours which escape from the electrolytic baths.

As a result the chromium electrolysis tanks must be equipped with a system to protect the workers from the vapours

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[+] cf. page 80 ff.

.../

containing no insignificant quantities of chromic acid (vesicular uptake) discharged into the atmosphere in the form of aerosols.

A collection and recycling system directly above the electrolytic bath is installed in certain shops.

It is estimated that the proportion of chromium deposited during chrome-plating is only 10 to 50 % in the case of decorative chromium and 25 to 90 % in that of hard chromium (on average 40 %),i.e. only 0.2 tonnes of each tonne consumed in one year in a shop reaches the chromium metal state during decorative chrome-plating and 0.4 tonnes during hard chromium plating, the remainder being lost (unless there are recovery systems).

Decorative chrome-plating is used on numerous metals, the principal base metal being steel (automobile trim, metallic surfaces with a super gloss finish). It is also used on zinc, brass and aluminium alloys. Plastics are also treated. Hard chromium is used more in the case of steels or aluminium.

Besides chrome-plating, electrolysis is finding its way into other fields, electrolytic polishing and deburring having enabled technical problems to be solved.

For example, electrolytic polishing of aluminium is performed in chromic acid baths (120 g/l) in the presence of H_2SO_4 and H_3PO_4.

The workpiece acts as the anode and its metal yields a salt with the acid solution. The cathode is formed by a substance that cannot be attacked in conditions known from experience.

The formation of aluminium ions and trivalent chromium calls for partial replacement of the baths at regular intervals (an excess or total absence of aluminium ions will detract from proper operation of the bath).

.../

TABLE 15

TYPES OF CONCENTRATED BATHS USED IN SURFACE TREATMENT ON DIFFERENT SUBSTRATES

Operation	Concentration of new bath		Spent baths	Discharge coefficient
	CrO_3 g/l	$Na_2Cr_2O_7$ g/l		
Pickling • Aluminium • Copper • Plastics	30 to 60 200 400 to 600		Changed periodically	( ) 0.8 to 0.9 (
Chromating or passivation	3 to 6	5 to 9	Changed frequently	0.8 to 0.9
Gloss finishing	150		Changed periodically	
Chrome-plating • Hard chromium • Decorative chromium	150 to 300		Changed after several years	( ) 0.25 to 0.9
Electrolytic polishing	120		Partial renewal	

.../

2.1.5 Estimation of chromium consumed in surface treatment shops:

Precise details as to the total number of surface treatment shops are not known. According to the INSEE 1974 list, 2300 establishments are recorded as "surface treatment shops". These are only the so-called "jobbing" shops, as the frequently larger "integral" shops linked with other activities are not accounted for.

The term "surface treatment" also includes shops simply carrying out painting work, but these do not concern the present study. It is thus difficult to evaluate the actual number of shops on the basis of the INSEE source.

Judging from a survey made at the Agences de Bassin, it seems that establishments performing surface treatments can be estimated at less than 3000. Only some of these shops, however, use chromic derivatives.
On the other hand, the surveys conducted by SERATRADI and FAIRTEC-FRANCE and the estimates of the Agences de Bassin made it possible for a rough evaluation to be made of the number of shops using chromium and the quantities consumed.

2.1.5.1 Results of in-depth investigations:

FAIRTEC-FRANCE and SERATRADI performed various studies in the following regions:

- Alsace (Bas-Rhin, Haut-Rhin);
- Lorraine (Ardennes, Meurthe et Moselle, Meuse, Moselle, Vosges);

.../

- Somme;
- Auvergne (Allier, Haute-Loire, Loire, Puy-de-dôme).

The investigations centred on nearly all of the shops in the 12 Departments looked into. The information obtained was classified in Table 16.

- Analysis of results:

- Total number of shops investigated: 433, 78 % integral shops;
- Shops using chromium derivatives: 168, i.e. 38.7 %;
- CrO_3 consumed: 307 tonnes (i.e. 160 tonnes of chromium).

If these results are to be extrapolated for the whole of France, it will seem justified to multiply the chromium consumption figures by a correction coefficient of 1.5. During the investigations, the various commercial products that may contain chromium could not be covered, giving rise to an underestimation of the consumption of chromium-containing products.

.../

TABLE 16

RESULTS OF INVESTIGATIONS: ALSACE, LORRAINE, SOMME, AUVERGNE

	Number of shops investigated			Shops using Cr	Consumption of CrO_3 in tonnes per year	Volume of spent bath Cr concentration > 10 g/l in per year
	Integral shops	Jobbing shops	Total			
Ardennes	(	(	36	16	8	400
Meurthe et Moselle	)	)	27	9	35	40
Meuse	(97	(17	12	4	17	250
Moselle	)	)	20	7	14	190
Vosges	(	(	19	4	12	600
Bas-Rhin	38	11	49	13	40	(1 500
Haut-Rhin	69	7	71	12	52	)
Somme	73	13	86	51	35	
Allier	13	3	16	(	4	530
Haute-Loire	7	1	8	)	2, 4	195
Loire	25	42	67	(52	82, 7	945
Puy de Dôme	20	2	22	)	5, 7	266
TOTAL	337	96	433	168	306, 8	≃ 4 700

...

Under these conditions, extrapolation would yield the following figures:

- Total number of surface treatment shops: 3400;
- Shops consuming chromium: 1350;
- Chromic acid consumed: 3600 tonnes (1850 tonnes of Cr).

The average discharge coefficient that is currently admitted for all surface treatment operations using chromium derivatives is 0.7 to 0.8, so losses could be estimated at 2700 tonnes of chromic acid (1400 tonnes of chromium).

As far as treatment is concerned, only the Auvergne investigation furnishes any information, so an extrapolation was not carried out. However, it is interesting to note the results.

Of the 52 shops using chromium, only 18 (approximately one-third) possess a treatment installation.

The table below and the histogrammes in Tables 17 and 18 give a breakdown of the results obtained in these shops provided with such equipment.

.../

Number of shops	Spent baths	Rinsing-eluate	
	Reduction CrVI neutralization	Reduction CrVI neutralization	Neutralization of sludges
1	X		
3	X		X
9	X	X	
5	X	X	X

As can be seen, 14 out of the 18 shops remove the chromates from all effluents containing CrVI, while 4 do so only in the case of spent baths.

Of these shops, 8 complete the treatment (disposal of sludges). 5 shops are provided with complete equipment (11 % of all shops).

This means that the bulk of the chrome passes into the environment in the form of CrVI.

The total volume of the spent baths of the 54 shops totals 1900 m^3 per year:

50 % are discharged directly into the environment,
50 % are detoxicated, 20 % of the detoxicated volume undergoing complete treatment with sludge disposal.

The rinsing water of the 54 shops totals 469 000 m^3:

70 % are discharged into the environment;
30 % are subjected to chromate-removal followed by neutralization, only half of the sludges formed being disposed of.

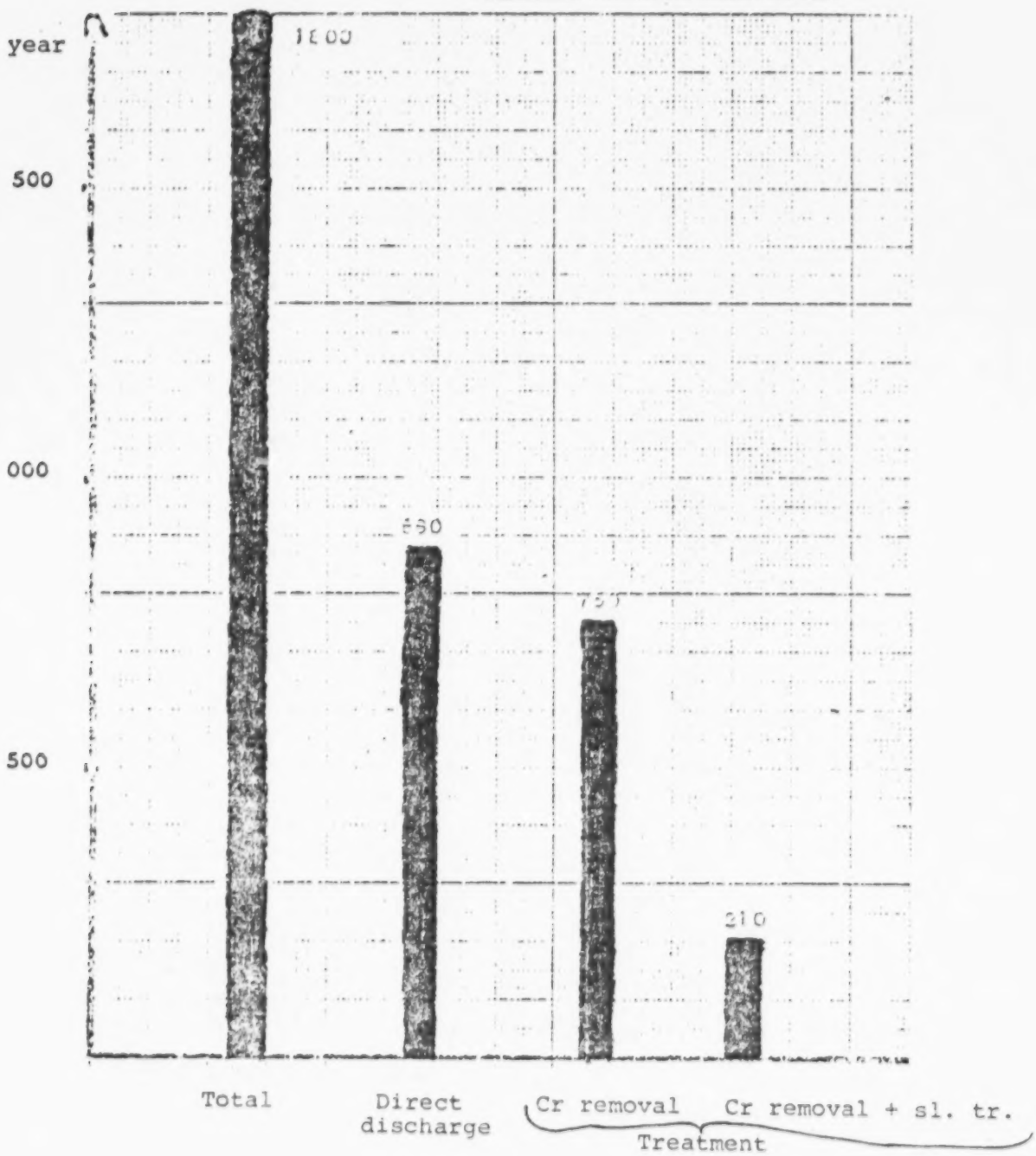
The problem presented by hexavalent chromium pollution thus justifies in-depth studies in each region.

.../

TABLE 17

DISTRIBUTION OF SPENT CHROMIC BATHS IN AUVERGNE

on the basis of disposal +

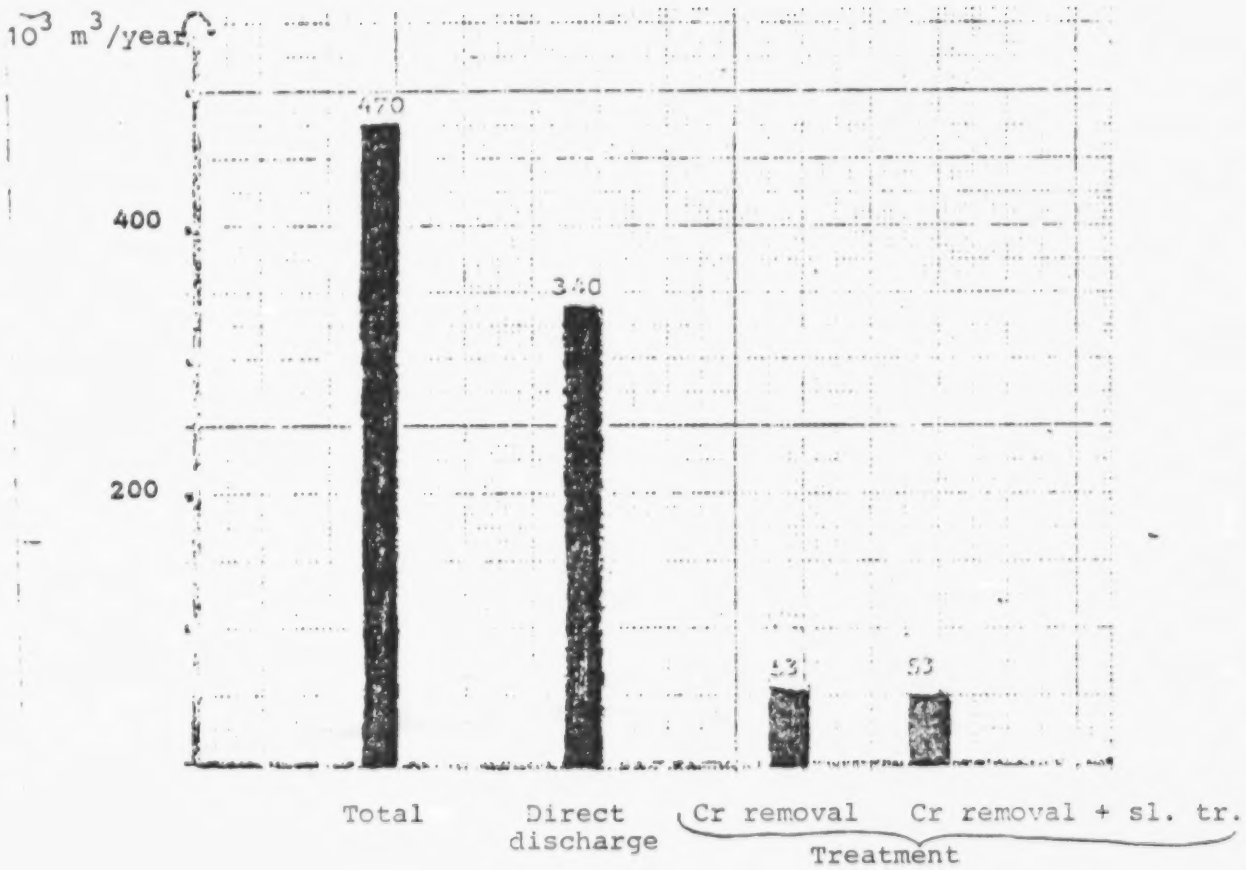


+ Table taken from the report "Traitement de surface" (Surface Treatment) drawn up for the Agence de Bassin Loire-Bretagne

TABLE 18

DISTRIBUTION OF CHROMIC RINSING WATER IN AUVERGNE

on the basis of disposal +



+ Table taken from the report "Traitement de surface" (Surface Treatment) drawn up for the Agence de Bassin Loire-Bretagne.

.../

2.1.5.2 Results of the investigation conducted at the Agences de Bassin:

The various Agences de Bassin were contacted so as to obtain further information.

Five of them furnished figures calculated by the Service des Redevances. The Agence de Bassin Rhône-Méditerranée-Corse has not yet analyzed the investigations made in the surface treatment sector. The Loire-Bretagne figures are merely an extrapolation made on the basis of the data collected by SERATRADI and FAIRTEC-FRANCE in Auvergne; the same applies to Rhin-Meuse (but with several corrections). Seine-Normandie and Adour Garonne could provide approximate figures very near to actual conditions. Artois-Picardie made a precise study of the sector and gives results that are accurate to within 5 %.

The various results are listed in Table 19 and Map 20.

.../

TABLE 19

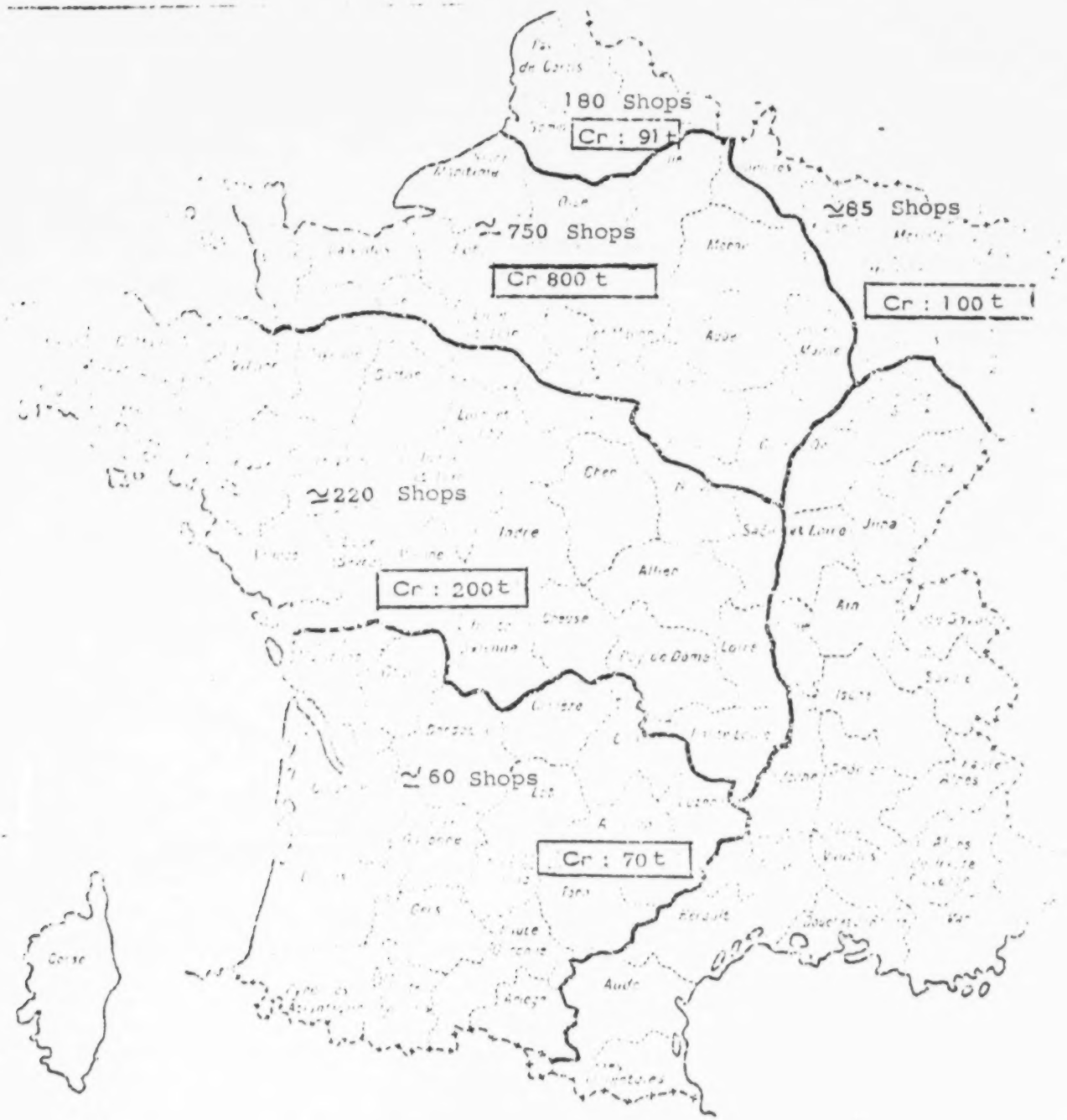
SURFACE TREATMENT SHOPS RECORDED BY THE AGENCES DE BASSIN

Agence de Bassin	Surface treatment shops	Shops using Cr		Chromium consumed	
		%		CrO_3 in tonnes	Cr (metal) in tonnes
Adour-Garonne	150	40 %	60	140	≃ 70
Artois-Picardie	170	46 %	79	180	≃ 90
Loire-Bretagne	400	55 %	220	400	≃ 200
Rhin-Meuse	300	28 %	85	200	≃ 100
Rhône-Méditerranée-Corse					
Seine-Normandie	1 000	75 %	750	1 600	≃ 800

.../

MAP 20

GEOGRAPHICAL DISTRIBUTION OF SHOPS USING CHROMIUM



.../

Although the results of the analysis being made in Rhône-Méditerranée-Corse are not known, it will be noted that the totals obtained are fairly close to those calculated on the basis of the regional investigations. However, the proportion of shops using chromium is higher - 59 % as compared with 40 % in the investigations. This is due to the very high percentage evaluated in Seine-Normandie.

As far as consumption is concerned, the tonnages are less than those put forward by extrapolation. However, the problem of special commercial goods containing chromium, which were not counted, is equally as important as in the investigations. The same coefficient of multiplication can thus be retained. Under these conditions the representative figure for CrO_3 consumption would approximate 4000 tonnes; this figure will be borne in mind when evaluating losses.

The total number of service treatment shops and shops discharging chromate effluents will be estimated at 3000 and 1500 respectively.

2.1.6 Conclusion:

As a function of the above-mentioned extrapolations, it can be estimated that the annual consumption of chromic acid in surface treatment will be roughly 4000 tonnes, to which 400 tonnes of dichromate must be added, making a total of about 2200 tonnes of chromium metal.

Estimating the chromium losses is a somewhat ticklish problem.

.../

It has been seen that there are several forms of discharge, which will be broken down into three types:

1. Spent treatment baths, high CrVI concentration > 10 g/l (10 to more than 300 g/l);
2. "Dead" rinsing baths, eluates after regeneration treatment of resins used in the treatment of rinsing water: average concentration 1 to 50 g/l;
3. Rinsing water, very dilute: CrVI concentration < 1 g/l.

A total of 4700 m^3 of concentrated or semi-concentrated baths was noted for 11 of the Departments investigated. Taking an average chromium concentration of 30 g/l, roughly 140 tonnes of chromium is arrived at in the waste, representing 1200 tonnes for the whole of France.

At a conservative estimate, the figure of 500 tonnes could be put forward for chromium discharged in the very dilute rinsing water; although the concentration is weak, a very large number of cubic metres of water is consumed, giving rise in the long run to major losses.

The hexavalent chromium discharged every year by surface treatment shops would thus total 1700 tonnes. The regional investigations showed that only 10 to 15 % of this waste is treated and transformed into non-toxic hydroxides or recovered for recycling. The final balance would show that 1500 tonnes of chromium VI are discharged every year into the environment.

.../

With a coefficient of non-utilization approximating 77 %

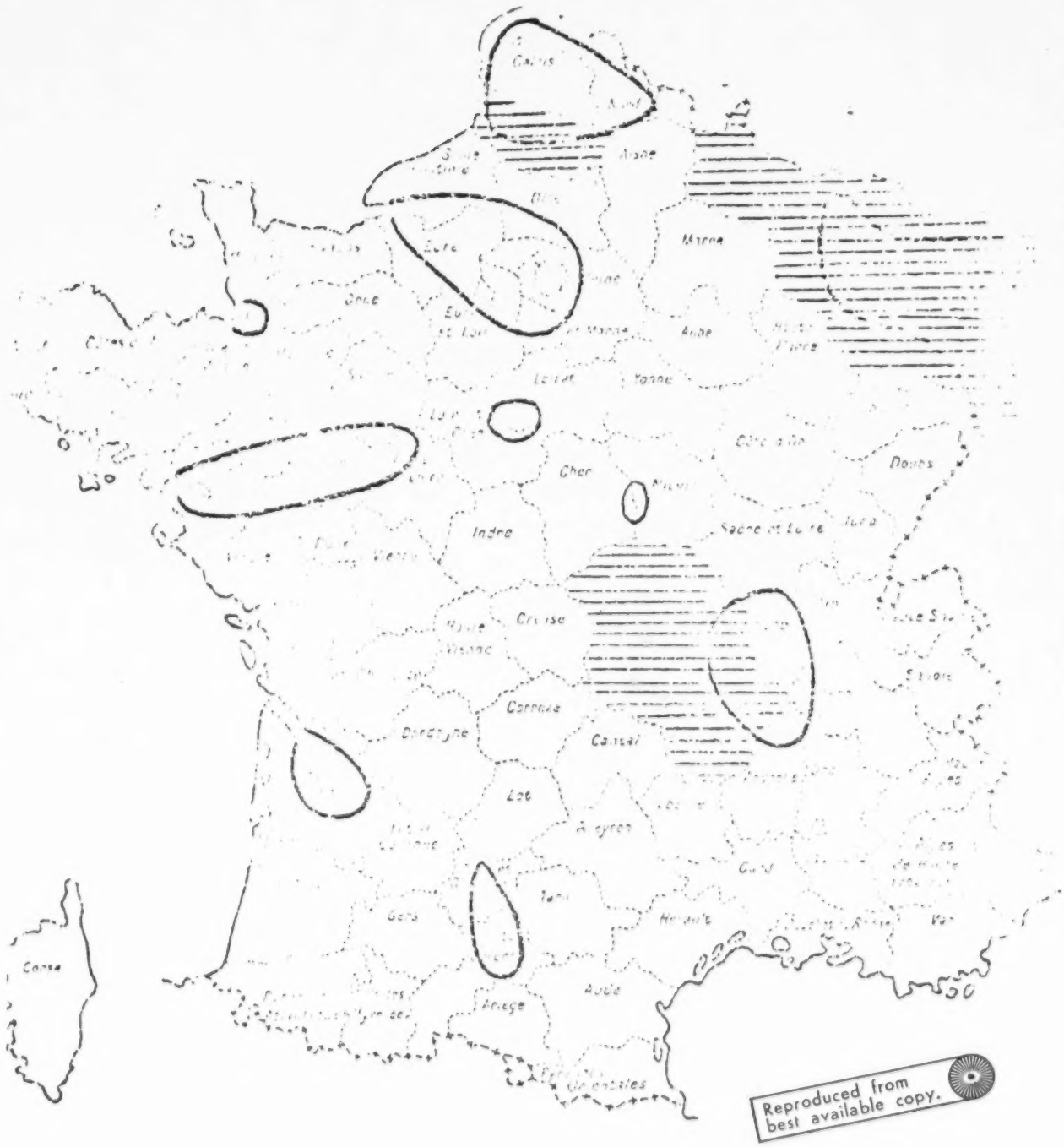
$$\text{(coefficient of non-utilization} = \frac{\text{chromium discharged}}{\text{chromium consumed}} = \frac{1700}{2200} = 0.77),$$

chromium from surface treatment shops is one of the major sources of pollution caused by chromium VI.

.../

MAP 21

GEOGRAPHICAL LOCATION OF SURFACE TREATMENT SHOPS WITH MAJOR CHROMATE EFFLUENTS



≡ Departments investigated

Geographical location of surface treatment shops consuming large quantities of chromium

2.2 Tannery:

After the end of the 19th century, the properties of chromium compounds were brought to light for tanning purposes. Two methods were developed almost simultaneously:

- the two-bath method, which is used today for goat or kid leathers;
- the one-bath method, which has gradually replaced the first method for all other types of leather.

• Two-bath method: the skins are first soaked in a slightly acidified sodium dichromate solution. Hydrated chromium oxide forms and soaks into the skin. However, it is above all during the second bath lasting several hours that the dichromate is reduced by the action of sodium thiosulphate in an acid solution. The chromium can then become fixed in the derm giving the leather a bluish colour. Numerous other reducing agents have been recommended: glucose, sawdust, neutral sulphite etc., but thiosulphate is used most in view of the favourable influence of sulphur on the suppleness of the leather.

After these operations, the skins are washed in water.

• One-bath method: the skins are mixed in a chrome alum solution (double chromium and potassium sulphate $\left[(SO_4)3Cr_2 \cdot SO_4K_2 \cdot 24H_2O\right]$) slightly neutralized by the addition of Na_2CO_3 and NaCl. The skin is introduced into several baths of increasing concentrations. The operation lasts between 6 hours and 2 days. In some cases a solution of dichromate and sulphuric acid, to which reducing agents such as glucose are added, are preferred to alum. The salts that have not been fixed are eliminated by washing out with water.

.../

There are numerous treatment conditions depending on the origin of the derms, their thickness and texture, and the future application of the leather. It is not, therefore, possible to give precise figures as to the concentrations of the various baths, which may vary from 2 to 25 g/l depending on the tannery, the average figure being roughly 6 g/l.

After tanning, the concentrated baths and skin washing water constitute the sources of pollution. Depending on the tanning method, the skins absorb between 60 and 80 % of the chromium used. Direct discharge of the concentrated baths or washing water gives rise to serious pollution as the chromium is in the hexavalent state (the concentration of this residual bath after tanning can be 10 g of Cr per litre).

Nevertheless, direct reutilization of the tanning bath is possible and often practised either for pickling or for actual tanning (after the chromium content has been increased); it is thus estimated that the average loss only totals 25 % (instead of 33 % in the case of non-reutilization).

.../

There are 69 tanneries throughout France (cf. Map 22).[+]

Tanning with chromium is said to account for 85 to 95 % of the various types of tanning and consume roughly 1700 tonnes annually[++] (expressed in chromium metal).

The average loss (25 %) would thus be 500 tonnes in the form of CrVI or CrIII (depending upon the above-mentioned methods employed).

Distribution of the tonnages of chromium losses involved in tanneries throughout France cannot be specified. However, Map 22 shows that four regions can be distinguished where tanneries are most frequently found:

Rhône-Loire; Limousin; Nord-Pas-de-Calais; Pyrénées Atlantiques,

which would give grounds to believe that above all problems of waste would be encountered.

[+] Information provided by the Chambre Syndicale des Cuirs et Peaux, Rue de Provence, Paris.

[++] Estimates furnished by "l'Ecole Française de Tannerie".

.../

TABLE 22

GEOGRAPHICAL LOCATION OF TANNERIES

.../

2.3 Chromium metal:

Chromium with a very high degree of purity is used in the fabrication of certain metal alloys. For this purpose chromium metal with a content of nearly 100 % is employed. Although its applications are typically of the metallurgical type, the production of chromium metal can justifiably be classified under chemical applications as chromium oxide is used as the basic substance.

It has been seen during the chrome-plating operations that the methods based on electrolysis enable a pure and brilliantly coloured metal to be obtained. This electrolytic method also yields very pure chromium used in the fabrication of alloys with non-ferrous metals.

Another method is employed: aluminothermics.

Reduction is carried out from chromium oxide Cr_2O_3 (obtained either directly from sodium or potassium dichromate or through chromic acid).

For this purpose a mixture of Cr_2O_3 (50 %) is prepared with aluminium powder (25 %) and chromic acid (25 %). Catalysts are added and the reaction initiated:

$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr.$$

The chromium metal gathers at the bottom of the crucible beneath the molten alumina and non-attacked chromium oxide. The purity of the metal is 97 to 99 % (the impurities being made up of Fe or Al).

Another method [+] uses silicon as the reducing agent.

$$2\ Cr_2O_3 + 3\ Si \longrightarrow 4\ Cr + 3\ SiO_2.$$

The chromium obtained is chiefly used in the fabrication of alloys with non-ferrous metals.

[+] Perrin Process. Masson, Volume II.

.../

Production in France is slightly more than 900 tonnes. Production losses in the crucible can be as much as 20 % and occur in the form of various chromium oxides discharged with the slag, which does not give rise to any pollution.

2.4 Pigments:

Chromium pigments are very numerous, the main ones being lead and zinc chromates.

- Lead chromates

The best known is chrome yellow $PbCrO_4$ which, depending on the type of preparation, gives a whole range of colours from lemon yellow to orange and red.

The reaction takes place between the sodium dichromate and a solution of lead salt, most frequently lead nitrate; lead acetate is, however, also used. Ceruse is employed to obtain chrome red.

The reaction, which proceeds to completion, does not take place with an excess of dichromate except for the formation of basic lead chromate ($PbCrO_4$; PbO).

$$2\ Pb(NO_3)_2 + Na_2Cr_2O_7 + H_2O \rightarrow 2\ PbCrO_4 + 2\ NaNO_3 + 2\ HNO_3$$

Some losses occur during filtration as a result of splashing (< 0.1 %). This also applies during conditioning. However, it can be said that the yield is nearly 100 %.

.../

- Zinc chromate

The basic salt in fabrication is generally zinc chloride; the reaction with the dichromate solution proceeds almost to completion. However, the zinc chromate is soluble in an acid medium, so part of the chromate dissolves during filtration as a result of the presence of chromic acid (pH < 7).

The chromium is entrained in the form of chromium VI and the losses in the effluents are less than 5 %.

French production of chromium pigments has been as follows:

	1973	1974
Lead chromate	6500 t	6900 t
(chromium)	(1050 t)	(1100 t)
Zinc chromate	500 t	130 t
(chromium)	(143 t)	(37 t)

For 1973 the figure of 7 tonnes of chromium VI is obtained assuming 5 % of losses in the fabrication of zinc chromate and neglecting any losses of lead chromate.

As in the case of the other chromium pigments (cf. Table 11), the use of lead and zinc chromates does not give rise to any pollution. Their various applications may be broken down as follows:

- Paints : 60 % ;
- Inks : 20 % ;
- Miscellaneous : 20 % ;
  (ceramics, tiles, cements, wall papers, plastics etc.)

.../

TABLE 23

PRINCIPAL CHROMIUM PIGMENTS

PIGMENTS	APPLICATIONS
Chromium oxide (Cr_2O_3)	Paint, ceramics, ink, glass
Guignet's green (Cr_2O_3, $2H_2O$)	Dyes, rubber, linen
Chromium sulphate	Paint, varnish, ink, porcelain
Lead chromate	Paint, enamels, ink
Lead chrome sulphates	Paint
Lead chrome molybdates	Paint
Lead silicon chromates	Paint
Zinc chromate	Fine paint, varnish, linoleum, rubber
Zinc tetraoxychromate	Primer on metals (replaces minium)
Barium chromate (lemon chrome)	Paint, ceramics, glass, porcelain
Bismuth chromate	Paint
Stannic chromate	Porcelain, earthenware
Manganese chromate	Water-based paint, porcelain, decoration
Ferric chromate	Paint, varnish, ceramics, porcelain
Ferric dichromate	Painting on cement, gum acacia
Chromium chlorate	Textile printing
Chromium orthophosphate	Paint

.../

MAP 24

GEOGRAPHICAL LOCATION OF PLANTS PRODUCING CHROMATE PIGMENTS, CHROMIUM SULPHATE, DICHROMATE, CHROMIC ACID ....

● Pigments

★ Other chromium compounds

...

There are few plants producing chromate pigments (cf. Map 24). The problem of effluents and waste thus remains very much a local problem.

2.5 Other chemical applications:

In addition to the above applications, which account for the bulk of the chromium, the following must be noted.

- Chemical oxidation - catalysis

In view of their high oxidizing capacity, chromium compounds are frequently used in both industry and laboratory practice for oxidation purposes. Above all chromic anhydride (CrO_3) or alkaline dichromate solutions with or without H_2SO_4 are used in the following cases:

- production of anthraquinone,
- oxidation of toluene to form benzoic acid,
- oxidation of cyclohexane to form acids used in the production of nylon and plastics, +
- production of vanillin, nicotinic acid, various aromatics,
- oxidation of aniline to form benzoquinone and hydroquinone,
- oxidation for bleaching oil, grease, wax,
- oxidation of sulphur to form thiosulphate,
- oxidation of arsenous anhydrides to form arsenates,
- production of vitamin B12.

During these operations the hexavalent chromium is reduced to trivalent chromium. Slightly more than 500 tonnes of chromium VI were thus employed in 1973 and discharged without any attempt at recovering them ++, chiefly in the trivalent form (including chromium sulphate).

+ PASCAL, Volume XIX: le chrome.

++ Recovery percentages are very low.

.../

As a catalyst, chromium is used in certain organic syntheses, such as in the production of methanol where chromium is associated with the zinc.

It is used as a reducing agent in certain organic production processes. For example, copper chromite $\left[Cu\ (CrO_2)_2\right]$ is used as a hydrogenation catalyst for alcohols and ketones. It is also used as a catalyst in the synthesis of sulphurous anhydride.

Numerous other compounds can be used as oxidizing agents or catalysts (cf. Table 25).

.../

TABLE 25

CHROMIUM COMPOUNDS USED IN REDOX REACTIONS

- Ammonium chromate $(NH_4)_2\ CrO_4$
- Ammonium dichromate $(NH_4)_2\ Cr_2O_7$
- Cesium chromate $CsCrO_4$
- Chromium oxychloride $CrC_{13} \cdot 6\ H_2O$
- Anhydrous chromium oxide (CrIII) Cr_2O_3
- Chromic acid (CrVI) CrO_3
- Copper - chromium oxide — hydrogenation catalyst
- Sulpho-chromic mixture — cleaning solution for glassware
- Lead chromate $PbCrO_4$
- Potassium chromate K_2CrO_4
- Chrome potassium sulphate $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 12\ H_2O$ — photography
- Potassium dichromate $K_2Cr_2O_7$
- Rubidium chromate Rb_2CrO_4
- Sodium chromate $Na_2CrO_4\ 4\ H_2O$
- Sodium dichromate $Na_2Cr_2O_7 \cdot 2\ H_2O$

.../

• Textile industry:

In this industry above all chromium "mordanting" is performed using chromates or dichromates, such an operation enabling better fixing of the dye.

• Hexavalent chromium mordants:

- sodium, potassium and ammonium dichromates,
- sodium, potassium, ammonium and manganese chromates,
- chromic acid.

The above compounds act as oxidizing agents and mordants. In this way wool is heat-treated in a dichromate solution, some of which is reduced to the hydrated chromium oxide state and fixed by the wool; the remainder acts as an oxidizing agent in the CrVI. The effluents contain CrIII (as CrVI is reduced).

• Trivalent mordants:

These are very numerous, the main mordants being chrome alum, ammoniacal chrome alum and chromium chlorate.

In 1973 effluents from dyeworks entrained roughly 5 tonnes of chromium in the CrIII form.

• Corrosion inhibitor:

Hexavalent chromium compounds are generally added in the form of dichromate plus a hydroxide (soda), in concentrations varying between 50 ppm and 2 %, to water in closed circuits (coolants, air-conditioning systems, automobile radiators, diesel locomotives).

The problem of disposing of the CrVI is encountered when it comes to draining the system, so these corrosion inhibitors are gradually being dispensed with.

.../

• Miscellaneous

Chromium and its compounds have many other secondary applications, including:

- photography (chrome alum for hardening and ammonium chromate as a sensitizer of the gelatin of photographic plates);
- photoengraving (ammonium dichromate);
- phytopharmacology ('moth-proof' chromium fluoride for wool);
- protection of wood against various parasites;
- electronics: Cr_2O_3 magnetic tapes;
- as a fuel additive to increase the rate of combustion.

Each of these applications gives rise to chromium pollution which is difficult to estimate but which is clearly less than pollution caused by surface treatments and tanneries.

Without claiming to be complete, the following causes of pollution can be listed:

- phosphate industries (Cr emission in flue gases);
- incineration of packing paper (in the form of lead chromate in the yellow ink used for printing on the exterior of packagings);
- burning of coal or petroleum;
- production and utilization of anti-rust additives;
- production of fireworks etc.

.../

3. Chemical applications of chromium - balance

The following balance sheet could be drawn up in 1973.

TABLE 26

Input		Production or utilization		Chromium losses (in tonnes)
Product (t)	Chromium content (t)	Product (t)	Chromium content (t)	
Chemical chromites		Sodium dichromate		
29 000	8 700	17 600	6 160	1 500
		Miscellaneous		
		unknown	unknown	unknown
Dichromate		(Chromic acid	unknown	unknown)
		) Chromium oxide	unknown	unknown (weak
		(Chromium sulphate	unknown	unknown)
Chromic acid and sodium dichromate	2 000	Surface treatment		1 700
Alum, sodium dichromate	2 000	Tannery		500
Chromic acid Dichromates Various salts		Oxidizing agents - catalysts		500
Chromium oxide	1 100	Chromium metal		200
Dichromates		Pigments		
		• Lead chromate		
		6 500	1 050	7
		• Zinc chromate		
		500	143	
Dichromates, chromates, chromic acid		Textile dyeing		5
				TOTAL LOSSES
				4 412 tonnes

The total losses of chromium are slightly more than half the chromium content of the 'input' chemical chromites. In most cases, adequate installations will allow losses and the ensuing pollution to be reduced.

Bearing in mind the imports and exports of the various chromium compounds (Table 27), a table can be drawn up summarizing the chromium losses in chemical applications (Table 28).

.../

TABLE 27

IMPORTS AND EXPORTS OF THE VARIOUS CHROMIUM COMPOUNDS

(in tonnes of cnromium)

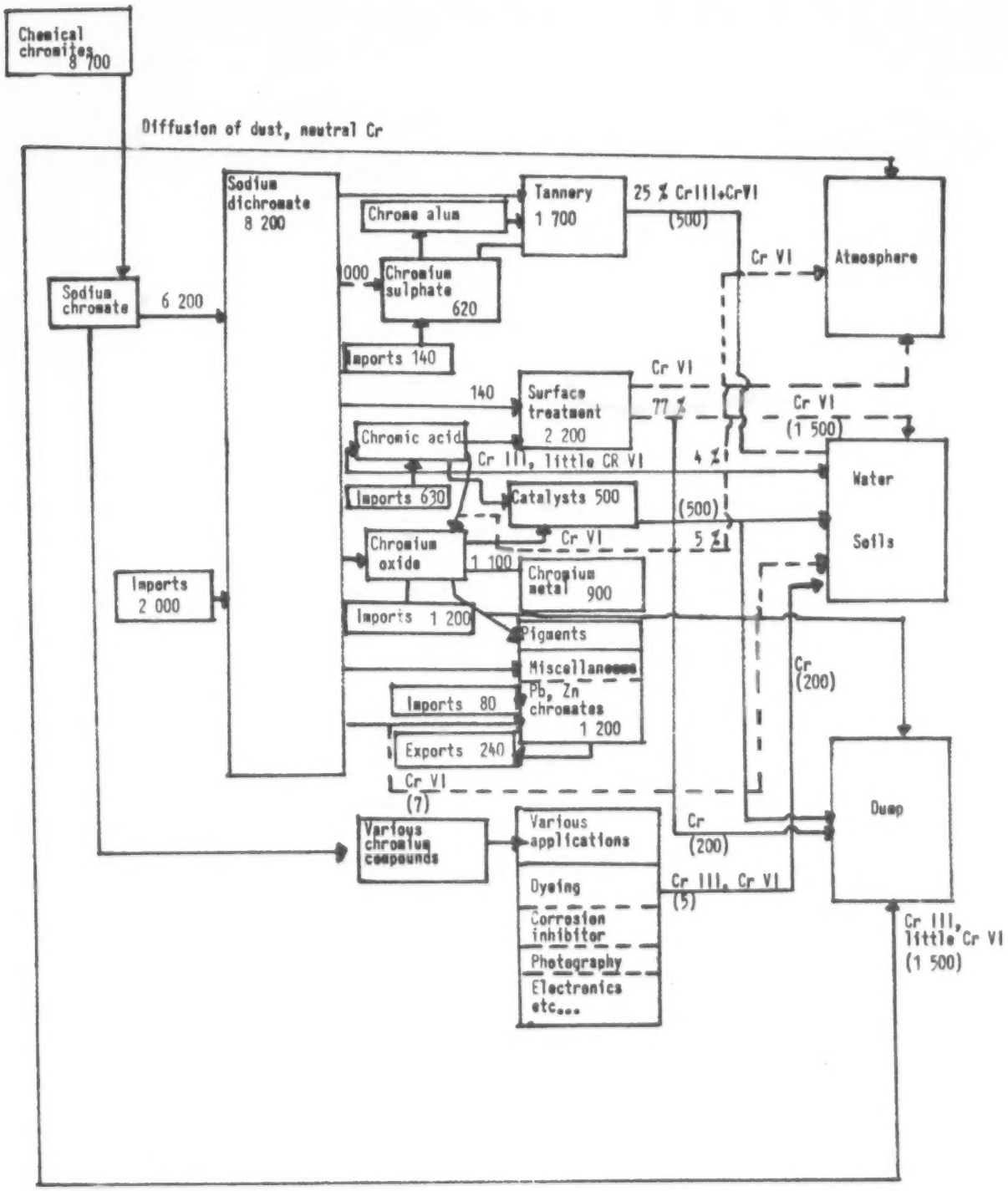
Product	Imports	Exports
Sodium dichromate	2 000	---
Chromic acid	630	---
Chromium oxide	1 200	40
Chromium sulphate	140	---
Pb and Zn chromates	80	240

.../

TABLE 28

SUMMARY OF CHROMIUM LOSSES IN CHEMICAL APPLICATIONS (1973)

(in tonnes of chromium)



+ Losses indicated in parentheses.

.../

C/ Refractory applications

All imported "refractory" chromites are used in the fabrication of refractory products, which may either be pure or mixed with magnesia or alumina.

The characteristics of refractory chromite can vary greatly depending on its future application. The Cr_2O_3 content varies between 10 and 35 %.

Pure chromite refractory bricks are chiefly used to line open-hearth furnaces. However, their gradual disappearance and the poor mechanical properties of chromite mean that such bricks are being used less and less frequently. These bricks, which withstand temperatures of roughly 1 600 to 1 650°C, improve resistance to thermal shocks (rapid change in temperature). They are obtained by binding the granulated chromite with a little refractory clay and roasting at high temperature.

Production has tended to aim more towards chromite-magnesia bricks, which are less expensive, have better properties, are more resistant to elevated temperatures (1 800°C in the case of magnesia) and still offer good resistance to thermal shock. The chromite and magnesia are mixed in variable percentages (20 to 73 % magnesia), then treated in the rotary furnace to obtain fritted magnesia-chromium. The product is then fed into a press with an organic binding agent and finally into a tunnel furnace, which completes the high-temperature roasting.

Losses occur at several stages:

- in the form of dust;
- during mixing;
- when the furnace is being charged;
- in the flue gases from the furnaces.

A collection system can be provided. The dust recovered

.../

enters the composition of the monolithic lining material, a floury chromite powder product used in the cold setting of ceramics or concrete.

Brick waste is formed during roasting. It is first crushed, then recycled at the mixing stage.

It is estimated that the refractory bricks have to be replaced after 400 furnace cycles; the lining is completely removed and mostly disposed of.

These bricks are chemically neutral and do not give rise to any pollution. The waste is revalorized in the production of second-choice bricks, which may be used in certain open-hearth furnaces.

From the pollution angle, therefore, the refractory applications of chromium do not present any problems.

.../

III NUISANCES INVOLVED IN THE UTILIZATION OF CHROMIUM

3.1 Toxicity of chromium

Elemental chromium is not found in a free state in nature, but rather in chromite, a chemically neutral ore in the form of stable chromium oxide (Cr_2O_3).

The natural chromium concentration of the marine environment is 0.04 µg/l.

By discovering various compounds and finding plenty of uses for them, Man has created a potential source of environmental pollution.

The direct toxicity of chromium to Man, fauna or flora has been studied. By way of contrast, when it comes to estimating long-term changes to an ecosystem or biotic cycle, numerous unknown factors are still encountered.

As was seen earlier, the distinction is made between two major types of chromium compounds: trivalent and hexavalent.

3.1.1 Trivalent chromium:

The toxicity of trivalent chromium has not been clearly established. However, it is known that an excessive concentration of CrIII in an aquatic environment disturbs the growth of certain algae (inhibitive effect) and can result in the death of shellfish or fish if it reaches too high a threshold. Wastewater sludges can be enriched in CrIII by up to 3 % of their dry weight without biodegradation of organic substances suffering.

The toxicity threshold of chrome salts with respect to bacteria is roughly 40 mg/l, while for algae of the Scenedesmus strain, it is roughly 4 mg/l.

.../

In Man, cases of dermatitis have been recorded following repeated contact with powder from the crushing of chromate-magnesia refractories during the production of the monolithic lining material. Although it is only absorbed with difficulty, trivalent chromium could accumulate in the epidermis and react with proteins in surface layers to form an "antigen-antibody" complex. However, such a complex disappears rapidly and the lesion normally heals without any recurrence.

3.1.2 Hexavalent chromium:

Hexavalent chromium compounds are, by contrast, known for their highly toxic action. These substances, which are very oxidizing and soluble in an acid medium, constitute a risk when absorbed by an organism.

The action of CrVI is poorly known. Like all toxic agents, it takes effect at cellular level either by acting on the enzymes (inhibition, stimulation) or by interference with oxygen-conveying elements (cytochrome oxydase).

Like all toxic agents, CrVI does not have any harmful effects until a certain concentration threshold has been exceeded. For instance, the average content of estuary algae in industrialized countries is roughly 1.4 ppm without any apparent damage. Precise work [+] performed on three strains of algae has shown that chromium inhibits growth for the following concentrations:

Strain of algae	Concentration with inhibitive effect (mg/l)
Scenedesmus	0.5
Navicula	0.1
Marocystis	1.0

[+] BROWNING - 1969 "Chromium in toxicity of industrial metals".

.../

The inhibitive effect is also joined by fixation, the consequences of which on the entire biological cycle vary depending on the strain and physico-chemical conditions.

The metallic components of wastewaters can have toxic effects on bacteria and other microorganisms involved in biological treatment processes. This applies to chromium VI; it accumulates in purification plants and detracts from proper operation.

CrVI impairs proper operation of these plants based on the principle of activated sludges and trickling filters (bacteria beds) at concentrations of 2 and 1 mg/l respectively. [+] (CrVI does not affect digestion of the sludges unless the concentration is greater than 200 mg/l).[+]

Aquatic fauna reacts in extremely different ways to the bio-aggressions of these metal compounds. Thanks to their keen senses, most strains avoid water zones with an excessive concentration of toxic substances, although this is first preceded by a certain degree of sensitization, and usually metal compounds are poorly detected.

Natural rates of fixation for chromium are approximately as follows [++]:

- lamellibranchiates 1 ppm;
- worms 10 ppm;
- fish $<$ 1 ppm.

The average LD_{50} varies between 20 and 200 ppm depending on the strain. The LC_{50} of potassium dichromate for daphnia is 1.2 mg/l (IRCHA).

At the present time the action of chromium in terms of reproduction and mutagenesis is unknown.

[+] Les eaux résiduaires industrielles - F. MEINCK, H. STOOFF Masson 1970

[+] BROWNING - 1969 "Chromium in toxicity of industrial metals'

Fish are relatively tolerant, while their food, plankton, is highly sensitive. The toxicity of chrome salts to plant life has been illustrated in the light of several species of plants. Solutions with a low CrVI and CrIII content have a bad effect on various cereals, tobacco and sugar beet. The chromium can reduce growth or cause the death of the plant. +

The toxic action can be diminished by using manure and fertilizer, but the poisoning of the soil cannot be eliminated.

Man is also sensitive to hexavalent chromium compounds. Such compounds cause irritations and corrosion; they can be absorbed through the skin or inhalation. They affect above all the skin and the respiratory tract.

Intoxications generally occur during industrial activities and in various cases:

- inhalation of micromists of chromic acid escaping from chrome-plating baths;
- inhalation of dust and vapours given off during dichromate production;
- cutaneous contact during the production or utilization of hexavalent compounds.

The most common complaints due to chromium VI are as follows +:

- ulceration: very common
  (corrosive action of chromium which enters through cuts)

+ Encyclopédie médecine, hygiène, sécurité du travail B.I.T. Geneva 1972

- dermatitis:
  - cutaneous irritation caused by contact with chromates
  - penetration of CrVI through the sweat-glands, reduction to CrIII;

    in the dermis, probable reaction with proteins through the formation of an antigen-antibody complex;

- severe effects on the respiratory tract:

  inhalation of dust or mists causing irritation of the mucous membranes;

- ulceration of the nasal septum:

  dust deposit giving rise to lesion;

- digestive disorders:

  repeated swallowing of small quantities of CrVI compounds can cause inflammations of the alimentary canal;

- delayed effects[+]:

  bronchial cancer could appear after prolonged exposure, sometimes several years after such exposure has ended.

Finally, the intake of considerable doses of CrVI compounds can be mortal for Man (case reported after 0.3 g of potassium dichromate were ingested).[++]

[+] Encyclopédie médecine, hygiène, sécurité du travail B.I.T. Geneva 1973 et Industrial hygiene and toxicology, Interscience Publishers 1962 - PATTY

[++] Précis de toxicologie - R. FABRE et TRUHAUT - Sedes Paris p. 672

.../

The toxic action of chromium on flora and fauna can lead to a scarcely perceptible degradation of the environment. Such degradation hardly ever appears "out of the blue" but rather in the long term coupled with the action of other toxic compounds. It may well be the source of lasting and dangerous disturbances in the ecosystem.

After this rapid survey of the nuisances that may confront the living world, the next natural step is to deal with the techniques used in reducing or eliminating the effects of such nuisances.

.../

3.2 Review of the various sources of chromium pollution

As seen earlier, the production of certain chromium compounds or their utilization in various branches of industry means that toxic waste is emitted.

Besides the distinction between trivalent and hexavalent chromium, the receiving body should be analyzed so as to obtain a more precise idea of the extent of pollution involved. Table 18 is designed to illustrate the composition of all wastes (CrIII or CrVI, physical state) on the one hand, and their receiving body on the other.

Chemical applications alone are the source of practically all waste containing trivalent or hexavalent chromium.

In general CrVI is found in effluents and is thus admitted into sewers or streams. Less frequently it is to be found in aerosols (production of chromium oxide, chrome-plating operations), its receiving body being the atmosphere. After utilization as an oxidizing agent or catalyst, it can be disposed of in a solid state.

CrIII is either disposed of in effluents or mixed with solid waste.

A wide range of techniques and methods will thus have to be developed so as to preserve waters, in addition to the atmosphere and the soil.

TABLE 29

VARIOUS TYPES OF CHROMIUM POLLUTION

Activity	Characteristics of waste			Chromium quantity (t)	Receiving body
	Physical state	Form	Average concentration		
Metallurgy					
· handling of ore	dust	neutral	----	4 600	atmosphere
· preparation of ferrochromiums	(dust	neutral	----	(1 850	atmosphere
	)(solid	neutral	----	)3 750	dump
· steel pickling	liquid	CrIII CrVI		400	collector plant
Chemistry/ production					
production of dichromate	(dust	neutral	----	(	atmosphere
	)solid	CrIII CrVI	----	)1 500	dump
	(liquid	CrIII CrVI	----	(	collector plant then dump
production of chromic acid	solid	CrIII	----	-----	collector plant then dump
production of chromium sulphate	liquid	CrIII	----	-----	collector plant then dump
production of chromium oxide	gases, fumes	CrVI	----	-----	atmosphere
production of pigments	liquid	CrVI	----	7	sewers, streams

VARIOUS TYPES OF CHROMIUM POLLUTION (cont'd)

Activity	Characteristics of waste			Chromium quantity (t)	Receivin body
	Physical state	Form	Average concen-tration		
• Chemistry/ utilization					
- surface treatment	liquid	CrIII CrVI		200 1 500	dump sewers, streams water ta
• concentrated spent baths	liquid	CrVI	10 to 300 g/l		
• semi-concentrated baths ("dead" washing baths)	liquid	CrVI	1 to 50 g/l		
• rinsing water	liquid	CrVI	< 1 g/l		
	gases, aerosols	CrVI	--------	-------	atmospher
- tannery	liquid	CrIII + CrVI	1.5 g/l	500	sewers, streams
- chemical oxidation catalysis	solid liquid	CrVI CrIII CrVI	--------	(500)	dump sewers, streams
- dyeing	liquid	CrVI, CrIII	--------	5	sewers, streams

+ Note: The chief form in which the chromium is present is underlined.

• In certain cases a "collector plant" was given as the receiving body; these are activities where it can be ensured that detoxication or regeneration treatment is performed.

.../

IV PREVENTION OF NUISANCES

The toxicity of chromium VI-containing waste was brought to light at the end of the 19th century in a dichromate plant.+ Preventive measures were thus taken rapidly in plants to avoid contact with chromium VI.

By way of contrast, it was only relatively recently that attention was devoted to the risks of pollution caused by effluents. At the present time chromium-containing effluents are not generally treated by all users. Certain branches of industry are more advanced than others, often due to the size of the companies at issue.

Technically, however, it is possible to treat all chromium-containing waters and to detoxicate them so that they are in line with the standards stipulated by the Ministerial Circular of July 1972.

4.1 Prevention techniques

4.1.1 Air pollution

The generation of a mist of chromic acid particles caused by hydrogen and oxygen given off during chrome-plating calls for the development of extraction and elimination systems for dust and mists containing hexavalent chromium. A device may be installed enabling chromium compounds to be retained and recycled to the electrolytic bath; otherwise, the mist is discharged into the air to assure dilution in the atmosphere.

The content of aerosols containing CrVI in the air must be monitored regularly by suitable detection instruments. The limit tolerated is 0.1 mg/m^3 of air for chromium VI compounds.

+ Ulcerations described by Cummings in 1887 in "Précis de toxicologie" René FABRE et TRUHAUT - Sedes Paris

Scrubbing must always be performed in shops where there is a risk of chromate dust settling.

Besides shops handling compounds containing CrVI, dust is scattered around unloading areas for chromite ores, possibly constituting a source of annoyance for the neighbourhood. To circumvent these drawbacks, the following methods have been employed:

- careful enclosing with exhaustion, dust extraction from the ore discharge points and transporters;
- spreading of the ore over the area and consolidation by means of a bulldozer;
- addition of wetting or surface-active substances to the powdery raw materials;
- protection from the major winds.

4.1.2 Water pollution

There is no lack of prevention techniques; these techniques differ depending on whether the effluents contain CrVI or CrIII. The hexavalent chromium recovered can be easily reutilized. Trivalent chromium has little chance of being used as such since before it is reutilized, it must undergo an oxidation process, which would be far too burdensome.

4.1.2.1 Hexavalent chromium

Hexavalent chromium stems from chromic acid, various dichromates or chromates.

.../

It is found in the form of chromate CrO_4^{--} or dichromate $Cr_2O_7^{--}$ ions.

Various methods are designed to eliminate these ions from industrial effluents.

a) Reduction and precipitation method:

This is a "destructive" treatment. CrVI is reduced to CrIII by reacting it with a reducing agent, which can be either SO_2 or bisulphite. The reaction takes place in a very acid medium, pH = 3 (obtained by adding sulphuric acid), in accordance with the following reactions:

$$3\ SO_2 + 2\ H_2CrO_4 \longrightarrow Cr_2\ (SO_4)_3 + 2\ H_2O$$

$$3\ H_2SO_4 + 6\ NaHSO_3 + 4\ H_2CrO_4 \longrightarrow 2\ Cr_2\ (SO_4)_3 + 3\ Na_2SO_4 \overbrace{\quad + 10\ H_2O \quad}$$

Other reducing agents are used under the same conditions: ferrous sulphate ($FeSO_4$), meta bisulphite ($Na_2S_2O_5$), hydrosulphite ($Na_2S_2O_4$), but these methods are less common. The redox reaction and pH can be checked by zero-current potentiometry.

After the reaction, the trivalent chromium obtained is eliminated by precipitation with lime or soda. Sometimes polyelectrolytes are used as agents to facilitate flocculation and treatment of the sludges.

This safe method enables residual hexavalent chromium contents of roughly 0.01 mg/l. It is used when the initial concentration of CrVI is high (> 100 mg/l).

.../

b) Solvent treatment (cf. Table 30):

The fundamental principle is based on the liquid-liquid extraction of concentrated CrVI solutions. This method enables CrVI to be recycled to the production of chromium compounds. The effluent is fed into an extraction column, where it is backwashed by a solvent which entrains the CrVI, bringing it to the front end. Once it has been separated from the solvent by alkalization with a sodium chromate solution, CrVI is decanted in the form of sodium dichromate in a reextraction tub. The sodium dichromate is recycled.

After having been washed to remove any remaining traces of CrVI, the solvent is cooled to 30°C and recycled to the extraction column.

The concentrated bath must present the following characteristics:

- CrVI > 25 g/l
- cations whose presence does not affect the process: CrIII, Fe, Al, Ni, Co, Pb, Si, Na, K
- cations whose presence can only be accepted after analysis: Cu
- cations whose presence is rejected: Hg
- indifferent anions: SO_4, PO_4 < 10 g/l, Cl < 1 g/l
- anions whose presence can only be accepted after analysis: F
- anions whose presence is rejected: I, Br
- pH: acidity of sulphuric acid
- suspended matter: none in the case of organic substances, for mineral substances < 10 g/l
- colouring substances: none.

Assuming that the bath corresponds to the following analysis:

CrVI = 26 g/l

SO_4H_2 = 210 g/l

the extraction yield of CrVI in such a bath would be greater than 99 %.

.../

It should be pointed out that although this method recovers virtually all the CrVI contained, the remaining CrVI must be destroyed downstream, in addition to the CrIII originally in the concentrated bath; the sulphuric acid must also be eliminated.

c) Anionic resin treatment:

The solutions containing CrVI pass over anionic resins. "Weak anionic" exchangers are employed, offering good resistance to oxidation; they are either of the macroporous or gel type with exchange capacities of 0.6 to 0.8 equivalent/l (one equivalent = 1 gramme molecular weight/litre, i.e. for Cr 30 to 40 g/l). The anions retained are eluated in the form of sodium chromate. Reduction is of the following type:

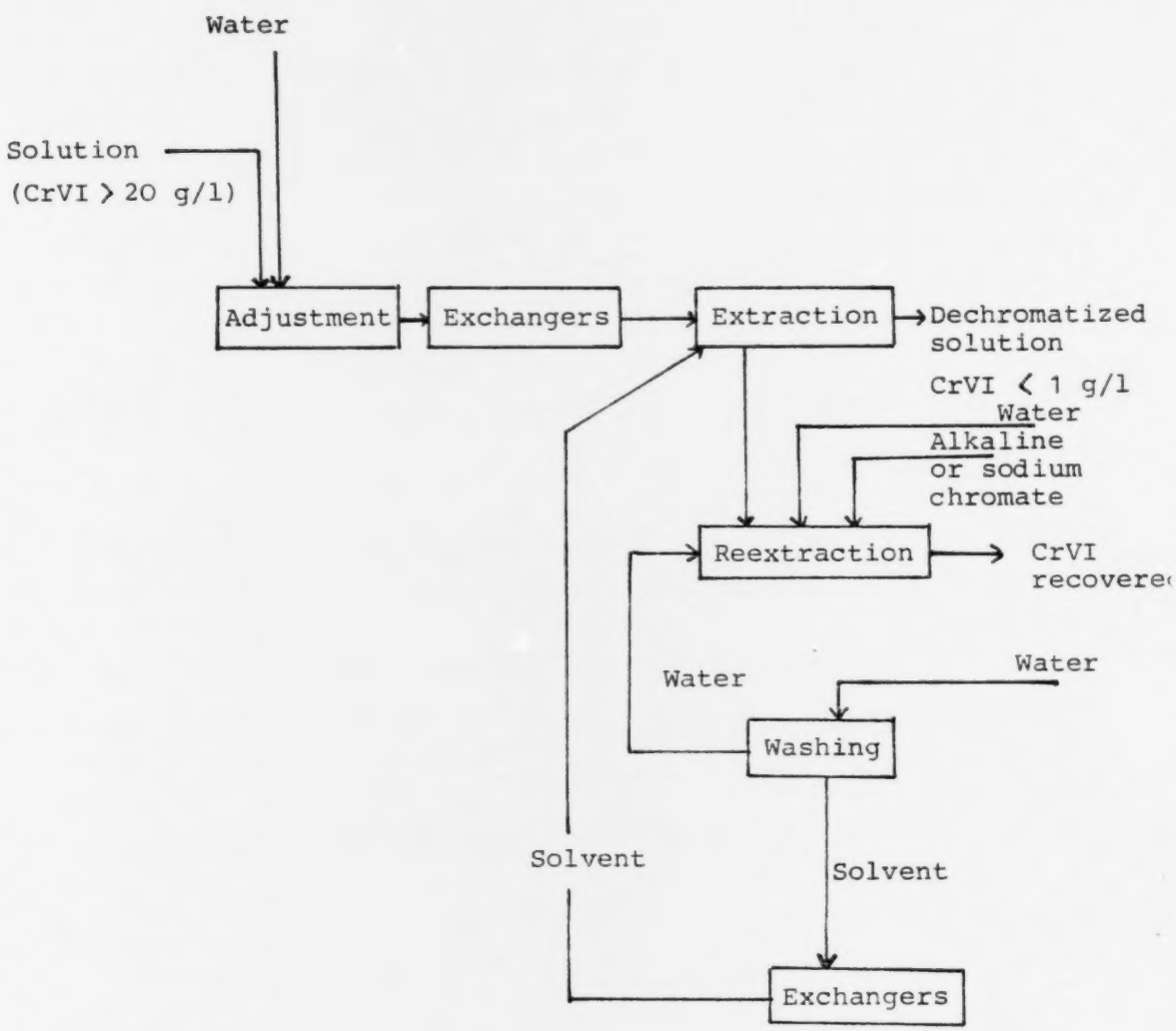
$$2\ R\text{-}OH + Cr_2O_7^{--}\ (\text{or } CrO_4^{--}) \rightleftharpoons R_2Cr_2O_7\ (\text{or } R_2CrO_4) + 2\ OH^-$$

This method is used for effluents whose CrVI content is 10 to 200 mg/l (e.g. rinsing water in surface treatment).

Once it has undergone homogenization, the effluent is decanted, filtered and then passed over the resin, in which the CrVI is retained. Once they have reached saturation, the resins are treated to be regenerated (it is projected to recover the CrVI by means of a detoxication unit).

TABLE 30

TREATMENT BY LIQUID-LIQUID EXTRACTION



d) Other treatments:

- Concentration by means of evaporation:

This method is used above all to concentrate a solution which can thus be fed into a liquid-liquid extraction installation. It is also applied to rinsing water in chrome-plating operations by means of selective vaporization of the water so as to concentrate the chromic acid, which in this manner can be reutilized in the electrolytic bath.

- Absorption via activated charcoal:

Experiments are still being carried out with this process, so no information can be provided.

- Concentration by means of freezing:

Experiments have been carried out in the USA and the process seems to be promising. +

4.1.2.2 Trivalent chromium

The distinction is made between two main methods of treating effluents containing trivalent chromium.

a/ Precipitation method:

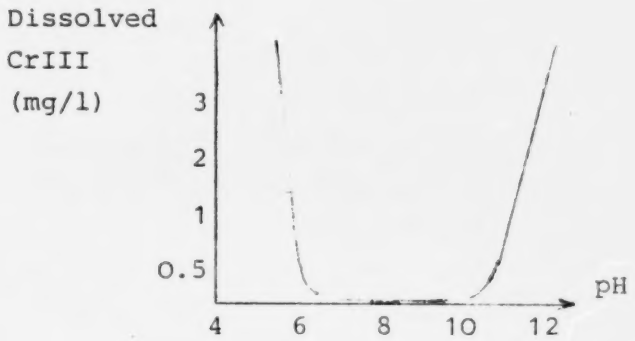
Whether stemming from the reduction of hexavalent chromium or trivalent compounds, CrIII can be treated in the same manner.

The precipitation method involves the formation of an insoluble chromium hydroxide $Cr(OH)_3$ by adding soda (NaOH) or lime (CaO).

+ Les rejéts métalliques d'origine industrielle en milieu marin, 3ème rapport périodique de l'A E O - May 1974

.../

The effluent is brought to a pH value of 8 - 9 (corresponding to the minimum solubility of the chromium hydroxide) (cf. curve below).



Solubility of chromium hydroxide as a function of pH.

The hydroxide precipitates slowly and incompletely. For this reason polyelectrolytes are used which improve precipitation and sedimentation. The sludges formed are difficult to dewater and their disposal causes problems. Various methods are used, including simple filtration, vacuum filtration and centrifuging. However, one of the best solutions seems to be the open-air decanting basin.

The dewatered substance can be disposed of. In view of the risk of pollution for groundwater through the entrainment of non-neutralized CrIII and CrVI ions, suitable natural sites or artificial areas are sought.

b/ Cationic resin treatment:

As trivalent chromium is positively charged, cationic resins are employed. At the same time as CrIII, the cations in the solution, including the iron and aluminium cations, are trapped on the resin and then eluated in the form of chlorides during regeneration of the resins.

.../

The reaction is of the following type:

$$3\ R - H + Cr^{+++} \rightleftharpoons R_3 - Cr + 3\ H^+$$

The chromic acid of the solution is thus purified, and its recycling is made possible. At excessive concentrations (> 250 g/l), the chromic acid attacks the resins; in this case the effluents must be diluted before treatment and the chromic acid recovered must then be reconcentrated prior to recycling.

This method, which is not as yet in general use, makes it possible for nearly all the trivalent chromium to be eliminated from the effluent and the chromic acid contained to be valorized.

CONCLUSION

The various treatment methods and techniques allow the CrVI content of the effluent to be reduced to concentrations of between 0.01 and 0.1 mg/l, which in most cases ensures that the waste meets current standards.

.../

4.2 Investments and operating costs

It was seen in metallurgical applications (cf. page 19) that plants are equipping themselves with dust extractors to treat the gaseous effluents.

In chemical applications tanneries discharge extremely mixed effluents which undergo global treatment. It is thus practically impossible to evaluate the share of chromium in general treatment.

As regards surface treatment shops, it is easier to furnish a few values representative of investments and operating costs.

For this purpose, the basis taken was medium-sized shops performing the most common types of surface treatments. The calculations made did not allow for the shops' structural or work modifications that might greatly reduce pollution as these modifications cannot be envisaged and assessed until a precise study has been made of each shop, which was not the objective at issue.

It will be appreciated under these conditions why efforts were not made to extrapolate the costs of pollution control to the whole of France, as the investment and operating cost figures at inventory level have merely an indicative value.

Chromium waste essentially stems from two types of surface treatment:

- electrolytic chrome-plating
- passivation of electrolytic deposits of zinc and cadmium,

which can be defined by an annual chromium waste flow.

.../

The distinction will be made between three treatments of this chromium flow, whatever its origin:

- individual installation for the detoxication of all effluents containing Cr^{6+};
- individual installation for the concentration of effluents by means of resins for the purposes of transferring and detoxicating the eluates in a collective centre;
- in situ detoxication by means of mobile resins regenerated in a collective centre.

In the latter two cases it is supposed that the proximity of a collective centre will enable eluates to be transferred and resins to be regenerated without any major consequences on the actual treatment costs.

4.2.1 Description of two medium-sized shops and determination of the pollutant level

It will be recalled that roughly 1 700 tonnes of chromium are discharged each year by some 1 500 surface treatment shops concerned in France, but approximately 800 tonnes are produced by a few dozen shops.

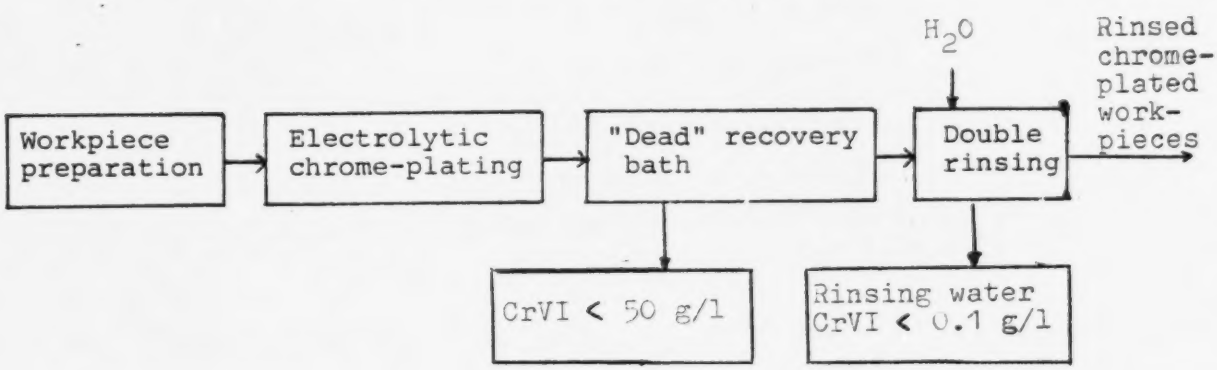
4.2.1.1 Chrome-plating:

Assuming that a shop performs electrolytic chrome-plating of workpieces in a classic electrolyte [+] and the capacity of the chrome-plating tank is several cubic metres, the surface of the workpieces treated daily can be roughly one hundred square metres.

[+] cf. composition, Table 15, page 45.

.../

The position occupied by CrVI waste in the treatment process is shown below in diagrammatical form:



The "dead" rinsing bath for the recovery of Cr^{6+} entrained by the workpieces at the electrolyte discharge can be enriched up to 50 g/l before being changed, and roughly 10 m^3 of rinsing water containing less than 0.1 g/l of Cr^{6+} can be collected daily.

The total annual pollutant flow of this shop would be roughly 200 kg of Cr^{6+}.

4.2.1.2 Chromic passivation of zinc and cadmium:

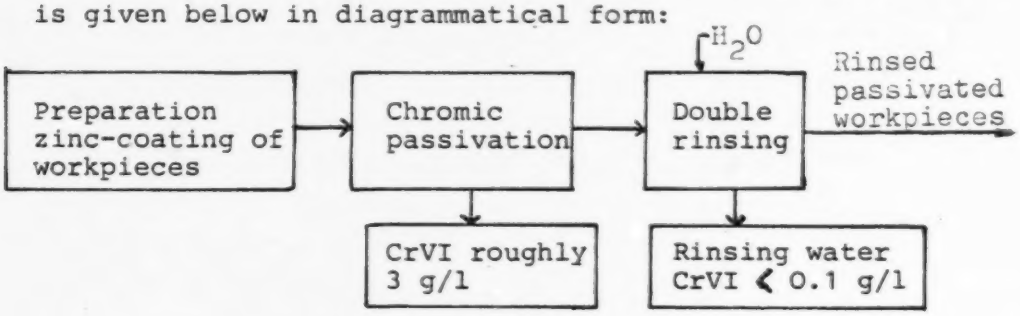
A look will be taken at a shop performing passivation of zinc-coated steel nuts and bolts in drums in a classic [+] passivating solution of low Cr^{6+} content (roughly 5 g/l).

Assuming that the number of zinc-coated and passivated parts is assessed at 200 drums daily each containing 40 kg of nuts and bolts, the volume of the passivation tank required will be 1 to 2 m^3.

[+] cf. composition, Table 15, page 45.

.../

The position occupied by CrVI in the treatment process is given below in diagrammatical form:



Cr^{6+} is removed from the passivating solution, which then becomes enriched with Cr^{3+} and must thus be replaced after several readjustments. In this shop 10 to 15 m^3 of rinsing water containing less than 0.1 g/l of Cr^{6+} are collected each day.

In the treatment of workpieces in drums, entrainment is such that a large part of the passivating solution is eliminated in the rinsing water.

The total annual pollutant flow of this shop would likewise be roughly 200 kg of Cr^{6+}.

4.2.2 Investments and operating costs

The three cases defined above (cf. section 4.2) will be examined in succession.

4.2.2.1 Individual installation for the detoxication of Cr^{6+} effluents:

The process is shown in diagrammatical form on page 103, the various stages or stations being described briefly and assessed in terms of investment and operating costs.

- Station 1: collection of effluents and storage.

- Station 2: detoxication, precipitation, flocculation, decantation:

  This includes the reaction tanks provided with agitators, level sensing contacts, electrodes and pH and rH sensors controlling the liquid intake and discharge solenoid valves.

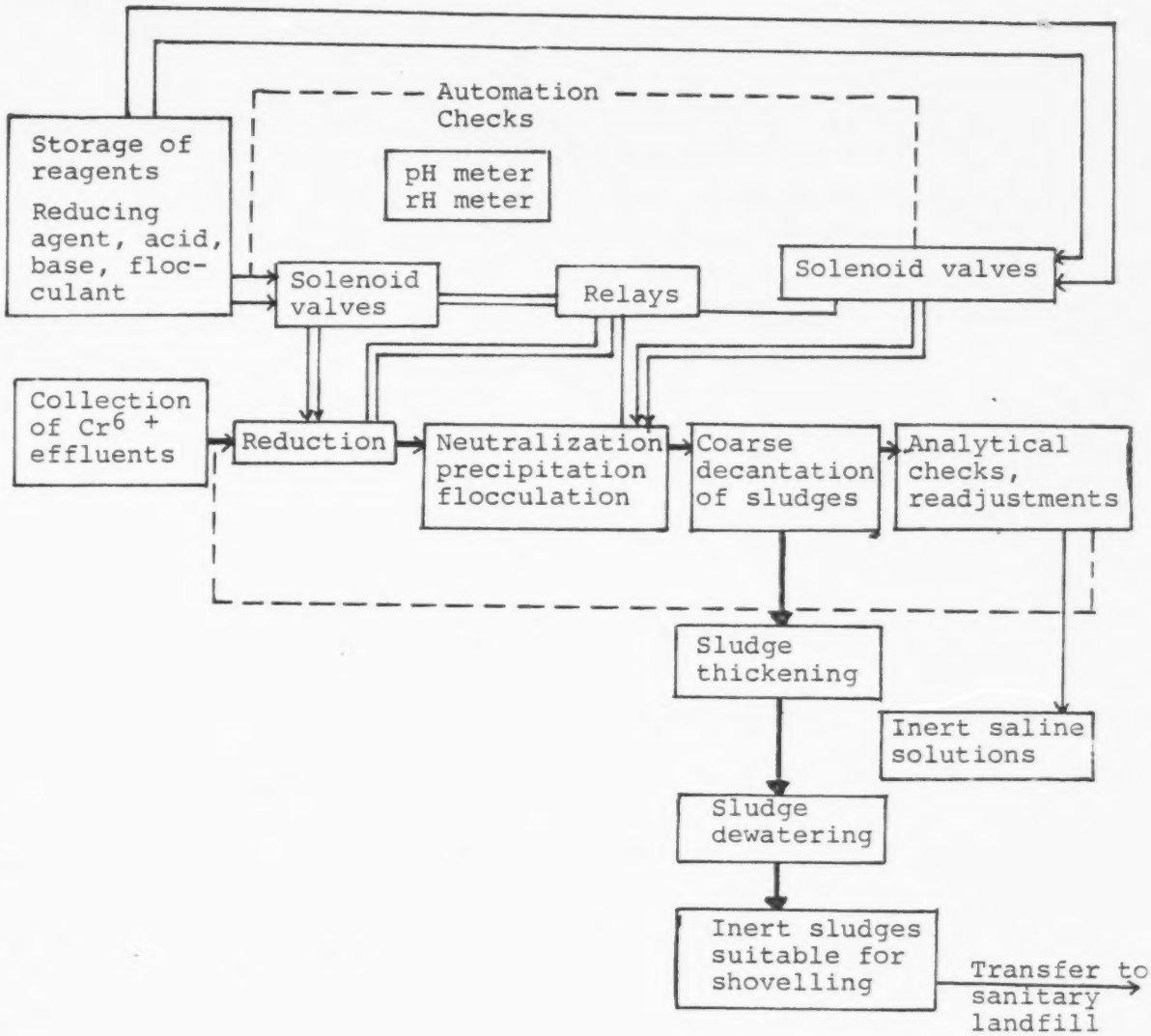
- Station 3: sludge processing:

  This station is for the processing of sludges which are dewatered after decantation and filtration, the filtration water being discharged in the installation and checked prior to discharge.

.../

TABLE 31

DESTRUCTION OF CrVI EFFLUENTS



.../

Realization of such a detoxication installation would call for investments of roughly 220 000 F (excluding tax).

The first two stations (collection/storage and destruction) account for 30 and 35 % respectively, while the third station (complete dewatering of the sludges) likewise accounts for 35 %.

The importance of the sludge processing station will be noted; the expenses involved in transferring the sludges suitable for shovelling to a nearby sanitary landfill must also be added.

The running costs also include the reagents, so the energy and labour expenses could total 20 000 F (excluding tax).

These figures must be interpreted with great care as the definition of the parameters of the various stations illustrates the possible variations existing from one shop to another (it should further be recalled that an analysis of the shop at this stage can show that reorganization would considerably reduce investments).

- Conclusion:

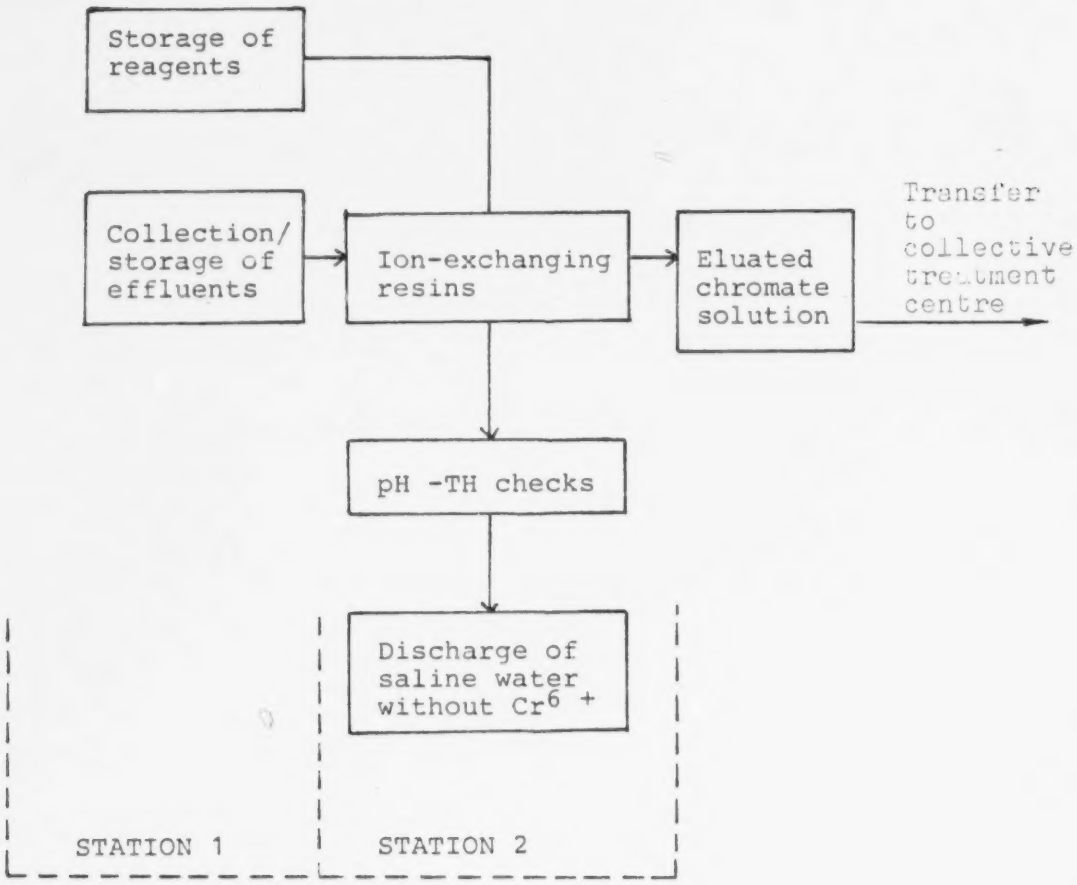
Investments	220 000 F (excluding tax)
Annual running costs	20 000 F (excluding tax)

4.2.2.2 Individual installation for concentrating effluents by means of resins for transfer of the eluates to a collective centre:

It will be recalled that the spent chromium solutions with concentrations of less than 0.1 g/l are passed through columns filled with anion-exchanging resins and that the eluates contain chromates in a sodium environment whose Cr^{6+} content is several grammes per litre.

.../

The theoretical schematic of the installation would be as follows:



Station 1: collection of effluents and storage.

Station 2: this station is represented by the resin columns and the systems for checking the quality of the water and regenerations. In addition to the anionic resin, a cationic resin must be provided to purify the water.

.../

investments for such an installation would be roughly 140 000 F (excluding tax).

The total running costs could be established as follows:

• Detoxication in a collective centre of roughly 50 m^3 of eluates (in accordance with tariffs approved by the Agences de Bassin)	50 m^3 x 220 F = 11 000 F (excluding tax) or 50 m^3 x 450 F = 22 500 F (excluding tax)
• Regeneration and maintenance of resins	5 000 F (excluding tax)
• Transportation of eluates over 50 to 100 km	60 F/m^3

Conclusion:

Investments	140 000 F (excluding tax)
Regeneration and maintenance of resins	5 000 F (excluding tax)
Costs of external treatment	14 000 / 25 000 F (excluding tax)

4.2.2.3 In situ detoxication by means of mobile resins:

Columns containing 250 litres of anionic resins, installed in parallel and operating alternately, are required. About twenty regenerations per year must be expected, i.e. 2 columns will be replaced every month.

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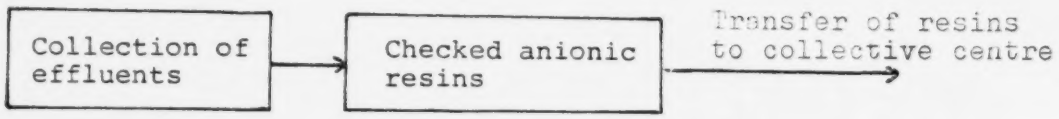
The schematic below represents the treatment stages:



Collection of the effluents can be evaluated at 50 000 F (excluding tax).

Purchase of the resin columns would cost 80 000 F (excluding tax).

Transfer and regeneration of the resins in a collective centre would cost 15 000 / 22 000 F per year (excluding tax).

- Conclusion:

Investments (collection of effluents, purchase of resin columns)	130 000 F (excluding tax)
Supervision of resins at shop site	1 000 F per year (excluding tax)
Transportation and regeneration of resins in collective centre	15 000 / 22 000 F per year (excluding tax)

.../

4.2.3 Financial balance sheet

Case	Investments F (excluding tax)	Running costs in shop F per year (excluding tax)	Cost of external treatment in collective centre F per year (excluding tax)
1	220 000	20 000	----------
2	140 000	5 000	14 000 / 22 000
3	130 000	1 000	15 to 22 000

As far as investments are concerned, figures are given that are felt to represent average prices with fluctuations of $\pm$ 10 to 30 %.

The shops, with all their imperfections, were "frozen" in terms of circuits and internal organization to provide guiding values for investments and operating costs, whereas in reality the circuits and surface treatment processes should first be reorganized so as to reduce the consumption of water and materials.

For a shop with an annual pollutant flow of less than 200 kg of Cr, total in situ detoxication treatment does not appear to be economical compared to systems for concentrating effluents by means of resins.

The choice between fixed and mobile resins depends on the possibilities of the shop in question. If a 250 l column is regenerated less than 12 to 15 times annually, the mobile resin method will be suitable.

.../

For a shop with an annual pollutant flow of more than 1 tonne of Cr, the in situ detoxication installation will be economical and, if coupled with resins, will further enable water savings.

On the other hand, investments involved in complete sludge processing call for a more detailed analysis as the minimum sludge rate for which the investments would be profitable is far higher.

4.2.4 Liquid-liquid extraction method

It was pointed out (cf. pp. 37, 94) that the liquid-liquid extraction method enables the recovery of the CrVI contained in concentrated baths, meeting the properties given earlier.

However, this method is only suitable for high tonnages of CrVI, which are beyond the reach of even the leading surface treatment shops.

In addition, this method does not seem to be suited for use in collective centres as to be economical, the tonnages of concentrated baths received would, expressed in recoverable CrVI, have to total at least 1 500 tonnes per year.

This amounts to supposing that the CrVI losses of all surface treatment shops, which we estimated at 1 500 tonnes, can be directed towards a single centre, which will have invested roughly 5 600 000 F in creating the liquid-liquid treatment unit. In this case the cost price of one tonne of CrVI recovered would total roughly 1 400 F excluding amortizations, overheads, financial expenses and effluent treatment expenses (cf. page 94), not to mention the expenses incurred in transferring all the concentrated baths to this single centre.

To conclude, it is felt that this method cannot be employed in a collective centre but rather in an industrial unit producing chromium derivatives, which is the case.

4.3 Existing or projected treatments in the industries analyzed (metallurgical and chemical industries)

There is no generally valid and standard detoxication method as the composition of the effluents varies from one industry to the next. The table below groups the various types of treatment used in the different industries reviewed.

Industry	Losses in the form of	Treatment used	% of shops performing treatment
Ferrochromium plants	Dust	• sheltered storage • sticky substances • dust extractors with fibreglass shafts	100 % (2 plants) (currently being equipped)
Stainless steel plants	Dust	Currently: liquid dust extractors	
	Pickling effluents (CrVI)	Reduction then neutralization with lime	100 %

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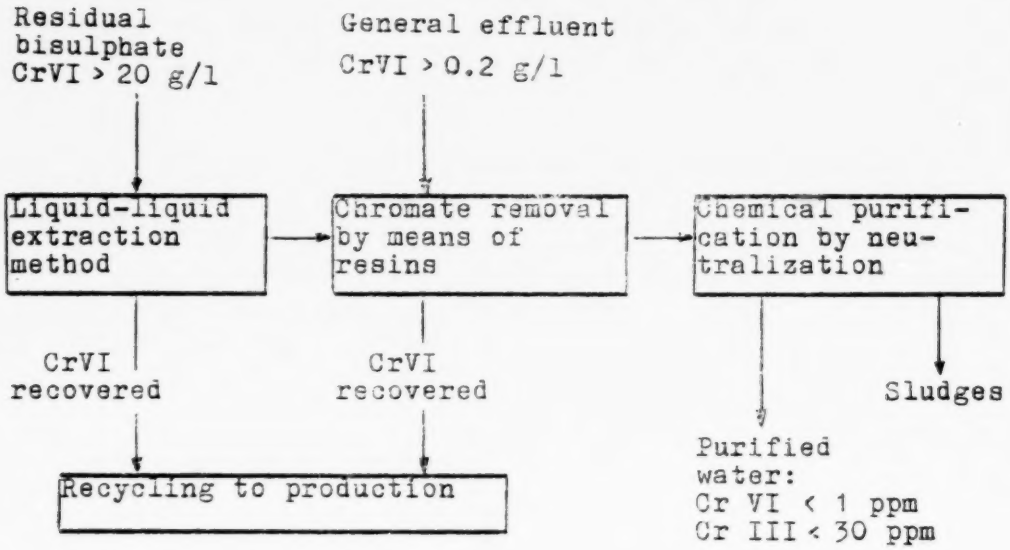
Industry	Losses in the form of	Treatment used	% of shops performing treatment
Chromium derivative plants	Production effluents (CrVI)	• liquid-liquid extraction process • chromate removal by means of resins • neutralization	Operational (1 plant)
Surface treatment	Effluents (CrVI)	• reduction (then neutralization) • fixed resins (then neutralization)	approx. 15 %
Tanneries	Effluents (CrIII or CrVI and other substances)	• reduction (then neutralization)	approx.20 %
Pigments	Effluents (CrVI)		
Oxidizing agents - catalysts	CrVI or CrIII		
Dyeworks	CrIII (CrVI)	• reduction (then neutralization)	

.../

While it was seen in the chapter on metallurgical applications that major efforts have been made, it appears that in certain industries listed in the chapter on chemical applications (e.g. surface treatment) there are still few detoxication installations excepting certain large surface treatment units. In the chemical group, an old plant of limited capacity and producing chromium derivatives has developed an advanced recovery system using various techniques for the detoxication or regeneration of the effluents in accordance with the general schematic shown below. Only the first phase, which enables far from insignificant recovery, has been effectively realized, while the two other phases are economically justifiable for major installations only.

TABLE 32

GENERAL SCHEMATIC OF CHROMATE EFFLUENT TREATMENT



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V PREPARATION OF A DISPOSAL PLAN

It follows from the data analyzed so far that the possible solutions to the problem of disposing of chromium waste are extremely varied. This is due to the scatter of the sources and diversity of the concentrations and treatment methods involved.

Preparation of a precise disposal plan thus seems to be a tricky job. Nevertheless, efforts were made in Table 33 (cf. page 118) to draw up a fundamental plan:

- Metallurgical applications do not produce any toxic waste, except during the pickling of chrome steels; the effluents undergo detoxication treatment before being discharged. The losses in the form of dust can be avoided by dust extractors and recycled to the preparation of chrome alloys; the slag containing inert Cr is dumped. These are, therefore, at all levels plant-internal treatments.

- The "Chemical applications" section analyzed tanneries, surface treatments, pigments, dyeworks and catalysts that produce concentrated, semi-concentrated or dilute effluents.

- Concentrated or semi-concentrated effluents:

  Such effluents are produced by surface treatment shops (1 200 tonnes of Cr) and tanneries (500 tonnes of Cr).

  They can be treated on the spot using the reduction-precipitation method or transferred to a detoxication centre. Only very large producers of chromium effluents would have any interest in setting up an individual detoxication station. Other producers would gain by sending their baths to a collective centre.

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- Dilute effluents:

Two solutions may be envisaged for surface treatment shops:

- concentration by means of resins followed by detoxication in the shop, or
- the eluate of the resins or the resins themselves are sent to a collective centre.

In the pigment and dye industries, only the second approach can be considered as the chromium waste flow is not significant. The quantities in question are roughly 500 tonnes for surface treatment, 7 tonnes for pigments and 5 tonnes for dyeing.

The problem of catalysts is different. These are most frequently in the solid state. Their treatment can be complex and is preferably performed in a collective centre.

- Role of the collective centre:

The collective centre receives the concentrated or semi-concentrated baths and detoxicates them using the reduction-precipitation method or performs recovery work. The sludges obtained are disposed of after dewatering, the water being recycled in the installations of the collective centre.

The sludges from individual treatments can likewise be transferred to a collective centre to be subjected to dewatering.

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On the basis of the various studies made by SERATRADI or FAIRTEC-FRANCE, it appears at the present time that in spite of all the possible reservations with respect to interpretation, a significant number of spent concentrated baths are available for possible transfer to collective centres. In addition, unitary systems for concentrating rinsing water would cause an increase in the volumes transferable.

There are at present two collective centres that are capable of detoxicating chromium effluents:

- Hombourg, near Mulhouse (Pec Engineering);
- Limay, near Mantes (S.A.R.P.).

It is projected to build other collective centres, in particular one in the Rhône-Alpes region (Plafora, cf. Map 34, page 119).

It is difficult to estimate whether these centres would be sufficient. An investigation would have to be carried out at national level comparable to that conducted in Loire-Bretagne to assess the potential market for effluents from surface treatment shops, including those containing CrVI.

Nevertheless, it can be seen from Map 34 that the two centres already in operation and the centre projected in the vicinity of Lyons are, from the geographical angle, able to play a leading role in the detoxication of concentrated and semi-concentrated chromium effluents.

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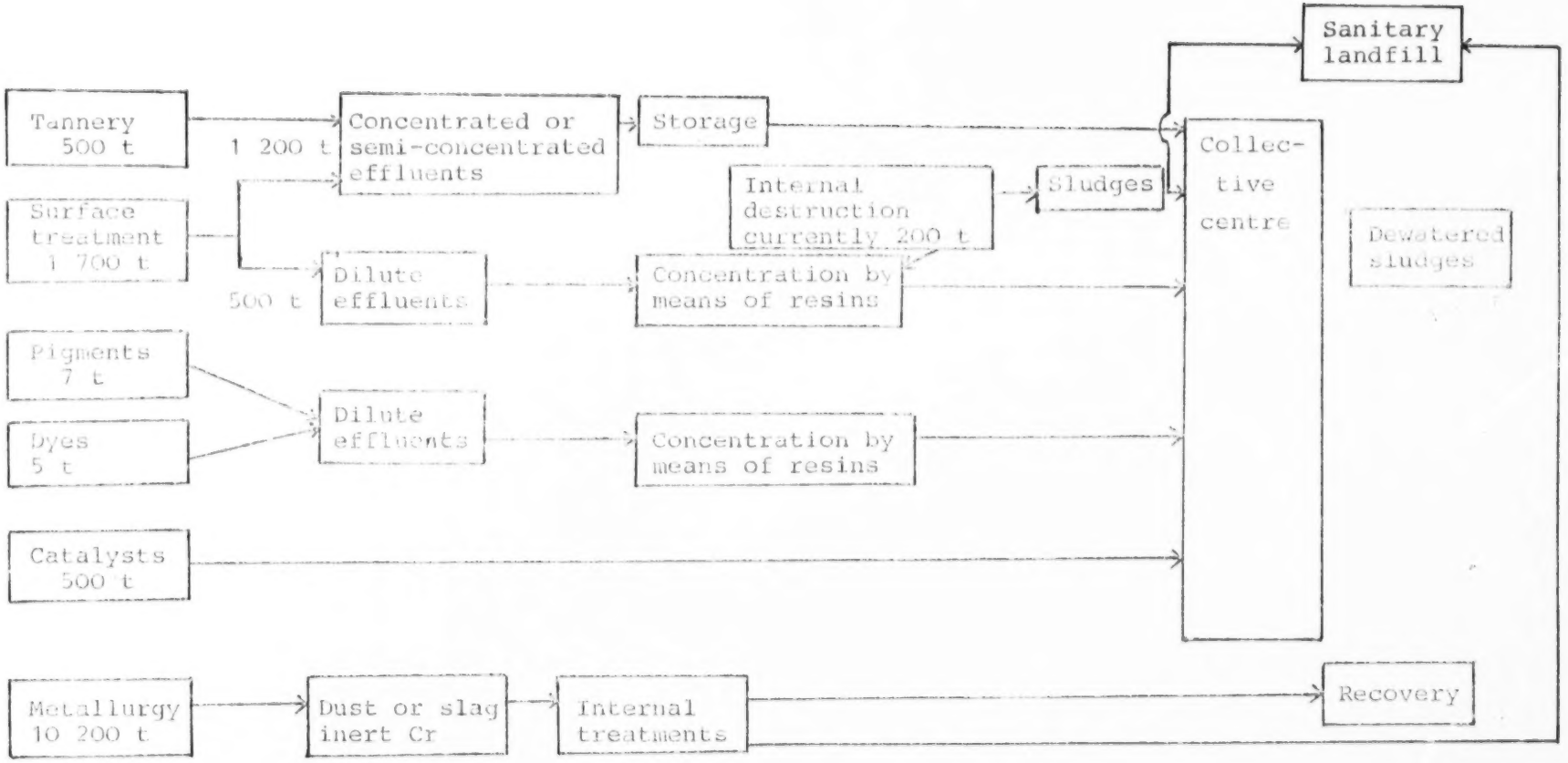
TABLE 33

DISPOSAL PLAN



MAP 34

COLLECTIVE DETOXICATION CENTRES: GEOGRAPHICAL LOCATIONS

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★ Collective centres for chromium detoxication, existing or projected

● Tanneries

▸ Pigments

◯ Geographical regions where surface treatment shops are located

VI GENERAL CONCLUSIONS

After the three major applications of chromium have been studied, the following conclusions can be drawn:

Chemical applications

Only these applications produce toxic waste containing substantial quantities of chromium in its hexavalent form.

- Occurrence: - surface treatment shops
  - tanneries
  - catalysts, pigments in small quantities.

Metallurgical applications

No toxic waste is produced. Losses occur essentially in the form of ores during handling or feeding into the furnace. The losses in the slag are also neutral with respect to the environment.

- Occurrence: - production of ferro-alloys.

Refractory applications

These applications do not give rise to any toxic waste. Chromium is incorporated in the form of chromite and the final result yields an insoluble product.

- Occurrence: - production of refractory bricks.

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When the tonnages in the above applications are quantified, it will be noted that surface treatment shops,with an estimated 1 500 tonnes,form the principal source of CrVI.

Part of the tonnage of chromium from tanneries and catalysts must be added to this figure - approximately a further 500 tonnes of CrVI.

2 000 tonnes of CrVI are thus discharged every year into the environment. This figure is sufficient in itself to justify major efforts to reduce it progressively and eliminate it altogether. We propose the following approach to keep in line with the direction requested by the Ministère de la Qualité de la Vie:

More precise knowledge of the tonnages of CrVI and locating of highly polluted regions.

For this purpose investigations such as those launched by the Agence de Bassin Loire-Bretagne would have to be conducted throughout France, efforts being made to situate with the maximum possible precision the share of pollution inherent to chromium.

Promoting in individual shops thus covered the setting up of units for the concentration of the most dilute chromium effluents through the use of ion-exchanging resins to trap the chromium and restore it to a more concentrated form, to be transferred to a collective centre or possibly recycled.

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Acceleration of the treatment (detoxication and possibly recovery) of chromium concentrates and semi-concentrates in collective treatment centres.

A programme such as this, which is incidentally beginning to develop in some regions, should be extended rapidly so that the sources of pollution in the most polluting sectors can be controlled.

In view of the present state of affairs and the lack of suitable information available, it seems to us to be impossible to put any figures to such a programme at national level. We indicated in section 4.2 guiding values as to the investment costs of individual units for the detoxication of chromium effluents. These purely indicative figures make it possible to situate the average costs to be provided for in the three cases considered. Any desire to perform an extrapolation to all shops would only yield a "mathematical" value, which will no doubt be a long way off from reality.

However, when the investigations which we recommend are conducted, it will be possible in each Agences de Bassin to assess more accurately the importance of the investments to be envisaged and evaluate the magnitude of the assistance - in individual shops - that the Agence de Bassin could furnish to such detoxication.

This assessment will also be made under consideration of the existence of collective centres without which, to our mind, a general plan on the detoxication of chromium effluents would be incomplete. The complementary relationship between individual treatment and collective treatment is demonstrated, as is obvious in our opinion, in the case of chromium effluents.

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